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A PROBLEM IN THE QUANTUM MECHANICS OF CRYSTALS

By E. L. Hill
University of Minnesota

(Received February 15, 1931)

Abstract

An elementary method is given for treating a one-dimensional lattice of the "tooth-valley" type containing any number of unit cells. The reflection of a beam of electrons from such a lattice is studied. For a semi-infinite lattice perfect reflection is shown to occur when the Bragg equation is satisfied, and an approximate formula for the widths of the reflection bands for high speed electrons is found. For the bound electrons the theory predicts occupied energy levels in the vicinity of the allowed levels for a single valley with infinitely high walls, in agreement with the perturbation theory. A simplified way of locating the edges of the reflection bands is discussed. The more complex case approximating real crystals is considered briefly.

Introduction

THE problem of determining the motion of the electrons in a crystal lattice has been treated by a number of authors. The usual method is to employ some type of perturbation scheme,[1] but the question has also been studied by the more direct procedure of replacing the crystal by a triply periodic field of force and then attempting the solution of the resulting equation for the characteristic function. Morse[2] has recently carried out this treatment in great detail, and has given many interesting results, but the mathematical technique is rather complicated and it is difficult to obtain a clear idea of the physical processes involved. Because of this it was suggested to the writer by Professor Frenkel that it would be interesting to try to carry through the calculation in detail for the case of a one-dimensional lattice of the "tooth-valley" type (Fig. 1). The work for this case is comparatively simple because the characteristic functions for the different sections of the lattice can be written down at once and then fitted together by use of the usual boundary conditions. A suitable method for handling the case of an infinite crystal is given in this paper.

[1] Sommerfeld, Zeits. f. Physik **47**, 1 (1928); Heisenberg, Zeits. f. Physik **49**, 619 (1928); Bloch, Zeits. f. Physik **52**, 555 (1928); Slater, Phys. Rev. **35**, 509 (1928).

[2] Morse, Phys. Rev. **35**, 1310 (1930). This paper contains references to previous work. Condon and Morse, Revs. Mod. Phys., **3**, 43 (1931).

Method and Calculation

The type of one-dimensional lattice considered is illustrated in Fig. 1. The valleys[3] are numbered consecutively 0, 1, 2, $\cdots$, n as is indicated by the letters in parentheses, the region $x<0$ corresponding to the 0th valley and the region $x>\xi$ to the nth valley. As there are just n teeth, $\xi=n\beta+(n-1)\alpha$.

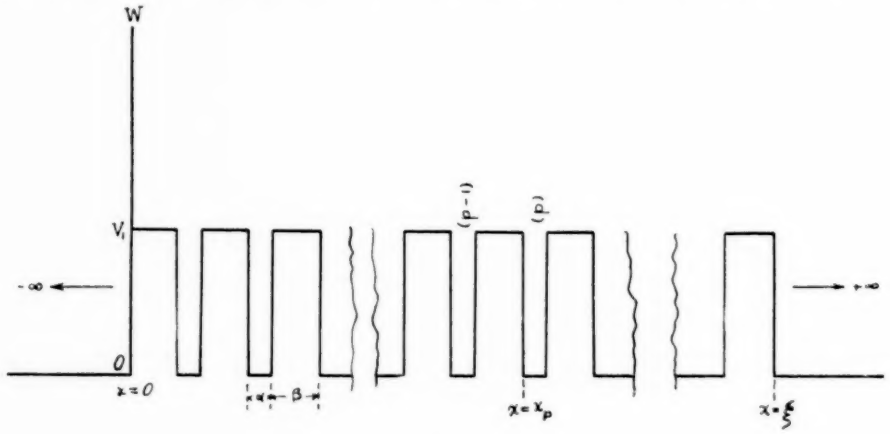

Fig. 1.

The plan is first to solve the Schrödinger equation for a lattice of n teeth and then let $n\to\infty$. The equation to be solved is

$$\frac{d^2\psi}{dx^2}+(8\pi^2m/h^2)(W-V)\psi=0. \tag{1}$$

In the pth valley the general solution of (1) can be written as

$$\psi = a_pe^{i2\pi k_1(x-x_p)}+b_pe^{-i2\pi k_1(x-x_p)} \tag{2}$$

and in the pth tooth, which lies between the $(p-1)$th and the pth valley, as

$$\psi = a_p'e^{i2\pi k_2(x-x_p)}+b_p'e^{-i2\pi k_2(x-x_p)}. \tag{3}$$

For[4]

$$x<0 \qquad \psi = Ae^{i2\pi k_1(x+\alpha)}+Be^{-i2\pi k_1(x+\alpha)} \tag{4}$$

$$x>\xi \qquad \psi = ae^{i2\pi k_1(x-\xi)}+be^{-i2\pi k_1(x-\xi)}. \tag{5}$$

where

$$hk_1=[2mW]^{1/2};\ hk_2=[2m(W-V_1)]^{1/2}. \tag{6}$$

In these equations it is explicitly supposed that $W\geqq V_1$ but it is well known that for $V_1>W\geqq 0$ the same equations can be used by giving k_2 its value as a pure imaginary number from (6).

[3] By "valleys" and "teeth" are meant, of course, the regions of low ($V=0$) and high ($V=V_1$) potential energy in Fig. 1.

[4] The extension to the case in which the wave number of the electron outside the crystal is $k_0<k_2$ is considered later.

At the boundary between a tooth and a valley we use the ordinary boundary condition of the continuity of ψ and its first derivative.[4a] By applying this condition to the function given by (2) and (3) one obtains a linear relation between the coefficients (a_p, b_p) and (a_{p-1}, b_{p-1}) of the form[5]

$$\begin{aligned} a_p &= c_1 a_{p-1} + c_2 b_{p-1} \\ b_p &= c_2^* a_{p-1} + c_1^* b_{p-1} \end{aligned} \tag{7}$$

where

$$\begin{aligned} c_1 &= (1/4k_1k_2)\{(k_1+k_2)^2 e^{i2\pi(k_1\alpha+k_2\beta)} - (k_1-k_2)^2 e^{i2\pi(k_1\alpha-k_2\beta)}\} \\ c_2 &= -(1/4k_1k_2)\{2i(k_1^2-k_2^2)\sin 2\pi k_2\beta\} e^{-i2\pi k_1\alpha}. \end{aligned} \tag{8}$$

Equations (7) permit one in principle to determine the coefficients in any part of the lattice provided they are assumed known in one valley, and in particular one can determine A and B in terms of a and b for use in Eqs. (4) and (5). In the present form this calculation is difficult because of the complicated character of c_1 and c_2. To simplify the analysis we introduce a new set of variables y_p and z_p by a linear transformation which is to be so determined that the transformation matrix from (y_{p-1}, z_{p-1}) to (y_p, z_p) is diagonal; i.e., y_p and z_p are to be simply multiples of y_{p-1} and z_{p-1} respectively. By this artifice we can at once compute A and B in terms of a and b after calculating the associated Y and Z in terms of y and z. We assume then

$$\left.\begin{aligned} a_p &= \gamma_{11} y_p + \gamma_{12} z_p \\ b_p &= \gamma_{21} y_p + \gamma_{22} z_p \end{aligned}\right\} \tag{9}$$

and on substituting in (7) we get as the condition that y_p and z_p shall be multiples of y_{p-1} and z_{p-1} respectively

$$\begin{aligned} \gamma_{11}/\gamma_{21} &= (c_1\gamma_{11} + c_2\gamma_{21})/(c_2^*\gamma_{11} + c_1^*\gamma_{21}) \\ \gamma_{12}/\gamma_{22} &= (c_1\gamma_{12} + c_2\gamma_{22})/(c_2^*\gamma_{12} + c_1^*\gamma_{22}) \end{aligned} \tag{10}$$

which is seen to be the condition that γ_{11}/γ_{21} and γ_{12}/γ_{22} shall be roots of the equation[6]

$$\tau = (c_1\tau + c_2)/(c_2^*\tau + c_1^*). \tag{11}$$

In general there are two different roots of (11) one of which must be taken for $(\gamma_{11}/\gamma_{21})$ and the other for $(\gamma_{12}/\gamma_{22})$ in order that the transformation (9) may be non-singular. These roots may be found directly from (11) if we set

$$c_1 = u + iv; \quad c_2 = \eta + i\zeta \tag{12}$$

with

$$\left.\begin{aligned} u &= (1/4k_1k_2)\{(k_1+k_2)^2\cos 2\pi(k_1\alpha+k_2\beta) - (k_1-k_2)^2\cos 2\pi(k_1\alpha-k_2\beta)\} \\ v &= (1/4k_1k_2)\{(k_1+k_2)^2\sin 2\pi(k_1\alpha+k_2\beta) - (k_1-k_2)^2\sin 2\pi(k_1\alpha-k_2\beta)\} \end{aligned}\right] \tag{13}$$

[4a] It is because of the character of the boundary condition that it is not necessary to give the precise value of the potential energy at the boundary between a tooth and a valley.

[5] A similar relation can readily be found connecting the coefficients (a_{p-1}', b_{p-1}') and (a_p', b_p').

[6] They are the invariant points of the linear fractional transformation $z' = (c_1z + c_2)/(c_2^*z + c_1^*)$.

$$\left.\begin{aligned}\eta &= -(1/4k_1k_2)\{2(k_1^2 - k_2^2)(\sin 2\pi k_1\alpha)(\sin 2\pi k_2\beta)\} \\ \zeta &= -(1/4k_1k_2)\{2(k_1^2 - k_2^2)(\cos 2\pi k_1\alpha)(\sin 2\pi k_2\beta)\}.\end{aligned}\right] \tag{14}$$

It may be noted that

$$|c_1|^2 - |c_2|^2 = (u^2 + v^2) - (\eta^2 + \zeta^2) \equiv 1, \tag{15}$$

which is also required by the condition that the current must be constant throughout the crystal and follows from the boundary conditions and the usual expression for the current.

The solutions of (11) are most conveniently divided into three classes according to whether $u^2>1$, $u^2<1$, or $u^2=1$ which we shall call Case I, II, and III, respectively. Denoting the two roots by τ_1 and τ_2 we get[7]

Case I. $u^2>1$

$$\begin{aligned}\tau_1 &= \{[v - i(u^2 - 1)^{1/2}]/(\eta^2 + \zeta^2)\}(-\zeta + i\eta) \\ \tau_2 &= \{[v + i(u^2 - 1)^{1/2}]/(\eta^2 + \zeta^2)\}(-\zeta + i\eta).\end{aligned} \tag{16}$$

Case II. $u^2<1$

$$\begin{aligned}\tau_1 &= \{[v + (1 - u^2)^{1/2}]/(\eta^2 + \zeta^2)\}(-\zeta + i\eta) \\ \tau_2 &= \{[v - (1 - u^2)^{1/2}]/(\eta^2 + \zeta^2)\}(-\zeta + i\eta).\end{aligned} \tag{17}$$

Writing $\gamma_{11}/\gamma_{21}=\tau_1$ and $\gamma_{12}/\gamma_{22}=\tau_2$ the transformation from y_{p-1} to y_p and from z_{p-1} to z_p is found to be

$$\begin{aligned}y_p &= (c_2^*\tau_1 + c_1^*)y_{p-1} = \delta_1 y_{p-1} \\ z_p &= (c_2^*\tau_2 + c_1^*)z_{p-1} = \delta_2 z_{p-1},\end{aligned} \tag{18}$$

where δ_1 and δ_2 are defined by (18) and can be found explicitly by using (16) and (17).

Case I. $u^2>1$

$$\delta_1 = u + (u^2 - 1)^{1/2}; \quad \delta_2 = u - (u^2 - 1)^{1/2} \tag{19}$$

Case II. $u^2<1$

$$\delta_1 = u + i(1 - u^2)^{1/2}; \quad \delta_2 = u - i(1 - u^2)^{1/2}. \tag{20}$$

By repeated application of (18) one can write at once for the relation between (Y, Z) and (y, z) which are associated respectively with (A, B) and (a, b),

$$y = \delta_1^n Y; \quad z = \delta_2^n Z. \tag{21}$$

Inverting (9) we find (A, B) from (Y, Z) and (a, b) from (y, z) and then from (21) find A and B in terms of a and b. The result is

$$\begin{aligned}A &= \left\{\frac{-\delta_1^n + (\tau_1/\tau_2)\delta_2^n}{(\tau_1/\tau_2) - 1}\right\} a + \left\{\frac{\tau_1(\delta_1^n - \delta_2^n)}{(\tau_1/\tau_2) - 1}\right\} b \\ B &= \left\{\frac{(1/\tau_2)(\delta_2^n - \delta_1^n)}{(\tau_1/\tau_2) - 1}\right\} a + \left\{\frac{(\tau_1/\tau_2)\delta_1^n - \delta_2^n}{(\tau_1/\tau_2) - 1}\right\} b.\end{aligned} \tag{22}$$

[7] Case III is treated in a later paragraph.

With the aid of these formulae we can now study the behavior of ψ as $n \to \infty$. We obtain the essential results, however, in a somewhat clearer fashion by studying the reflection and transmission properties of the grating.

Reflection and Transmission

To study the reflection of a beam of electrons from the grating assume that $b=0$ so that to the right ($x>\xi$) there is only a progressive wave to the right while for $x<0$ there is an incident and also a reflected beam. The reflection coefficient is then

$$R_n = \left| B/A \right|^2 = \left| (1/\tau_2)(\delta_1^{2n} - 1) \right|^2 / \left| \delta_1^{2n} - (\tau_1/\tau_2) \right|^2 \tag{23}$$

as from (19) and (20) $\delta_2 = 1/\delta_1$.

Case I. $u^2 > +1$.

From (19) δ_1^2 is real and >1, and from (16) and (17) $|\tau_1| = |\tau_2| = 1$. Hence from (23)

$$\lim_{n \to \infty} R_n = 1. \tag{24}$$

Thus whenever $u^2 > 1$ there is perfect reflection from the semi-infinite lattice, although not from a finite crystal. From (22) we find the limiting relation[7a] between A and B

$$A = \tau_2 B. \tag{25}$$

It is quite easy to find the characteristic function in any part of the crystal by inverting the transformation (22) and replacing a and b by a_p and b_p and δ_1^n and δ_2^n by δ_1^p and δ_2^p respectively. The determinant of the transformation is readily shown to be $+1$ (for any p) and on inserting (25) one finds

$$a_p = \tau_2 \delta_2^p B = \tau_2 b_p, \tag{26}$$

the characteristic function in the pth valley being

$$\psi = \left\{ \tau_2 e^{i2\pi k_1 (x - x_p)} + e^{-i2\pi k_1 (x - x_p)} \right\} (\delta_2^p / \tau_2) A. \tag{27}$$

A similar expression can be found for the pth tooth.

This result brings out very clearly the difference between a lattice bounded on one side only, and a lattice which is unbounded in both directions.[7b] In the former case[4] there exist solutions of (1) which are finite at $x = \pm \infty$ for all values of W, whereas in the latter case there are no non-vanishing solutions finite at both $+\infty$ and $-\infty$ when the electron energy is such that $u^2 > 1$. This is to be compared with Morse's method in which the function is written in all cases as

$$f(x) e^{i2\pi kx} \tag{28}$$

where $f(x)$ is periodic with period $(\alpha+\beta)$, the "forbidden" energies being associated with complex values of k. This function does not represent the gen-

[7a] Note that from (22) this relation must be satisfied in order that $|a|$ and $|b|$ may remain finite as n becomes infinite.

[7b] We shall distinguish these as "semi-infinite" and "infinite" lattices respectively.

eral solution of (1) as we must assume a relation between a_p and b_p in order that our solution (2) and (3) may be put in this form. It has not been possible as yet to show that the regions of complex k in (28) are identical with energies for which $u^2>1$. As $|\delta_2|<1$ we see that ψ is damped out within the lattice, $|\psi|^2$ being diminished approximately by a factor $|\delta_2|^2$ in a distance $(\alpha+\beta)$.

Case II. $u^2<1$.

From (20) δ_1 is complex and $|\delta_1|=1$. Let

$$\theta = \tan^{-1}[(1-u^2)^{1/2}/u];\ \delta_1 = e^{-i\theta}$$
$$-\pi < \theta < \pi,\ \theta \neq 0.$$

Substituting for τ_1 and τ_2 from (17) in (23)

$$R_n = \frac{(\eta^2+\zeta^2)\left[\dfrac{\sin n\theta}{\sin\theta}\right]^2}{1+(\eta^2+\zeta^2)\left[\dfrac{\sin n\theta}{\sin\theta}\right]^2} < 1. \tag{29}$$

This expression is always less than unity and as $n\to\infty$ it does not approach any limit but merely oscillates. In particular if θ is commensurable with π there are always values of n for which it is zero. There is no obvious reason for this type of "resonance" in terms of a fitting up of the electron wavelength with the lattice distances.[8]

Case III. $u^2=1$.

This case must be considered separately for as $\tau_1=\tau_2$ (9) is a singular transformation, the preceding analysis does not apply. Its treatment is not entirely unambiguous as there are two limiting processes to be considered; i. e. the simultaneous passage of n to infinity and the behavior of R_n in the neighborhood of $u^2=1$. For a semi-infinite crystal as we approach a point for which $u^2=1$ passing through values of W for which $u^2>1$, the limiting value of the reflection coefficient is unity. To find the limiting value by traversing points for which $u^2<1$ we may use (29) which yields

$$n^2(\eta^2+\zeta^2)/[1+n^2(\eta^2+\zeta^2)] \tag{29'}$$

where it is supposed that n has some finite, although large value. On allowing n to become indefinitely large we again get unity unless $\eta^2+\zeta^2=0$, which can occur only as a very special case since it implies $u^2=1$ and at the same time $\sin 2\pi k_2\beta=0$ from (8).

It is worthwhile to notice another method which offers a natural way of arriving directly at the formula for the positions of these reflection band edges From (16), (13), (14) and (15) we see that when $u^2=1$

$$\tau_2 = \pm e^{i2\pi k_1\alpha}$$

[8] Cf. R. d'E. Atkinson, Zeits. f. Physik **64**, 507 (1930).

the sign depending on whether $v>0$ or <0. (27) then becomes

$$\psi = (\pm)^p \left\{ e^{i2\pi k_1(x-x_p-a/2)} \pm e^{-i2\pi k_1(x-x_p-a/2)} \right\} e^{i\pi k_1 a} A,$$

where the upper or lower sign in $(\pm)^p$ is taken according to whether $u=+1$ or $u=-1$. As a similar equation can be shown to hold for the teeth we see that the energies for which $u^2=1$ are characterized by the fact that the wave function can be written in the form of a standing wave in each valley and tooth. Moreover, the amplitudes in two consecutive valleys (or teeth) are the same or of opposite sign depending on the sign of u, there being no damping out of the function within the crystal. In the next section it is shown that the even ordered Bragg reflections occur when $u>+1$ and the odd ordered when $u<-1$, so that for the former the characteristic function is approximately the same in consecutive valleys (or teeth) while for odd orders it is approximately the same except for reversal of sign.

This standing wave method was used by Professor Frenkel in his lectures, under the impression that it would pick out electron energies at the centers of the reflection bands, whereas it actually locates the edges. Knowing this, the method can be used to give the results of this paper for widths of the bands, etc.

Study of the Function $u(W)$

"Free" electrons. k_1 and k_2 real and positive.

By use of (13), u can be written in either of the forms

$$\begin{aligned} u &= +1-(1/2k_1k_2)\left[(k_1+k_2)^2\sin^2\pi(k_1\alpha+k_2\beta)-(k_1-k_2)^2\sin^2\pi(k_1\alpha-k_2\beta)\right] \\ &= -1+(1/2k_1k_2)\left[(k_1+k_2)^2\cos^2\pi(k_1\alpha+k_2\beta)-(k_1-k_2)^2\cos^2\pi(k_1\alpha-k_2\beta)\right] \end{aligned} \tag{30}$$

from which we see that $u>+1$ if

$$(k_1-k_2)^2\sin^2\pi(k_1\alpha-k_2\beta) > (k_1+k_2)^2\sin^2\pi(k_1\alpha+k_2\beta), \tag{31}$$

and $u<-1$ if

$$(k_1-k_2)^2\cos^2\pi(k_1\alpha-k_2\beta) > (k_1+k_2)^2\cos^2\pi(k_1\alpha+k_2\beta). \tag{32}$$

While it is not easy to specify precisely the values of W for which (31) or (32) is satisfied, it is clear that they are respectively satisfied in the immediate neighborhood of energies such that

$$k_1\alpha+k_2\beta = s \text{ or } s+\tfrac{1}{2} \tag{33}$$

where s is a positive integer.[9] If we define the wave-length of the electron inside the lattice as

$$\lambda = (\alpha+\beta)/(k_1\alpha+k_2\beta) \tag{34}$$

then (33) is just the Bragg reflection condition for normal incidence. This analysis is incomplete as we have not taken account of the fact that the aver-

[9] The order of the reflection is $2(k_1\alpha+k_2\beta)$ and is just the number of "wave-lengths" contained in $2(\alpha+\beta)$.

age potential in a crystal is negative with respect to the surrounding region, but the expression for the reflection coefficient can be readily set up when the wave number of the electron outside the crystal ($x<0$ and $x>\xi$) is k_0, where $k_1>k_2>k_0\geqq 0$, and on passing to the limit $n=\infty$ it is easily seen that perfect reflection still occurs when $u^2>1$. The wave-length of the electron outside the lattice is then λ_0 with

$$k_0 = [2m(W - V_0)]^{1/2}/h = 1/\lambda_0$$

the "index of refraction" being

$$\mu = \lambda_0/\lambda$$

the Bragg condition reduces to

$$s\lambda_0 = 2\mu(\alpha + \beta)$$

in agreement with the simple theory for the case of normal incidence.

Within the regions of validity of (31) and (32) reflection is perfect, so that for given values of α and β one can determine graphically the breadths of the reflection maxima. We can get a rough estimate of the breadths for large energies where k_1 and k_2 are large and approximately equal. For simplicity suppose $\alpha=\beta$, and consider especially (31). Noticing that k_1, k_2 and $\sin \pi (k_1-k_2)\alpha$ are slowly varying quantities compared with $\sin \pi (k_1+k_2)\alpha$ and assuming that the reflection band is approximately symmetrical about the point for which $(k_1'+k_2')\alpha=s$ we can let $k_1=k_1'+\Delta$ and $k_2\leqq k_2'+\Delta$ where Δ is small and is to be chosen such that (31) becomes an equality. To quantities of first order in Δ we get

$$2\pi\Delta s = \pm (k_1' - k_2') \sin \pi(k_1' - k_2')\alpha$$

but as

$$(k_1' - k_2') = (2mV_1/h^2)/(k_1' + k_2') = 2mV_1\alpha/sh^2$$

this yields

$$\Delta \backsimeq (mV_1\alpha/\pi s^2h^2) \sin [2\pi m\alpha^2V_1/sh^2]$$

or for the width on the energy scale

$$(\Delta W) \backsimeq 2k_1'\Delta h^2/m \backsimeq (k_1' + k_2')h^2\Delta/m \backsimeq (V_1/\pi s) \sin [2\pi m\alpha^2V_1/sh^2]$$

which, apart from the trigonometric term varies inversely as the order of the reflection. A similar result is obtained from (32). This result seems to be in general agreement with other calculations.[2,10]

"Bound" electrons. k_1 real and positive, k_2 pure imaginary.

Let

$$k_2 = ik = i(2m(V_1 - W))^{1/2}/h.$$

Although not of importance in electron scattering experiments this region is of

[10] L. Brillouin, Journ. de Physique (7) 1, 377 (1930).

interest in the theory of metallic conduction. From (30) u is expressed in terms of hyperbolic functions[11]

$$\begin{aligned} u &= +1-(2/k_1k)\left[k_1(\cosh\pi k\beta)(\sin\pi k_1\alpha)+k(\sinh\pi k\beta)(\cos\pi k_1\alpha)\right] \\ &\quad\times\left[k(\cosh\pi k\beta)(\sin\pi k_1\alpha)+k_1(\sinh\pi k\beta)(\cos\pi k_1\alpha)\right] \\ &= -1+(2/k_1k)\left[k(\cosh\pi k\beta)(\cos\pi k_1\alpha)-k_1(\sinh\pi k\beta)(\sin\pi k_1\alpha)\right] \\ &\quad\times\left[k_1(\cosh\pi k\beta)(\cos\pi k_1\alpha)-k(\sinh\pi k\beta)(\sin\pi k_1\alpha)\right]. \end{aligned} \tag{35}$$

This shows that $u<+1$ if

$$\left\{\begin{array}{l}\tan\pi k_1\alpha > -(k/k_1)\tanh\pi k\beta \\ \tan\pi k_1\alpha > -(k_1/k)\tanh\pi k\beta\end{array}\right\}$$

or if

$$\left\{\begin{array}{l}\tan\pi k_1\alpha < -(k/k_1)\tanh\pi k\beta \\ \tan\pi k_1\alpha < -(k_1/k)\tanh\pi k\beta\end{array}\right\}$$

and $u>-1$, if

$$\left\{\begin{array}{l}\tan\pi k_1\alpha > (k/k_1)\coth\pi k\beta \\ \tan\pi k_1\alpha > (k_1/k)\coth\pi k\beta\end{array}\right\}$$

or if

$$\left\{\begin{array}{l}\tan\pi k_1\alpha < (k/k_1)\coth\pi k\beta \\ \tan\pi k_1\alpha < (k_1/k)\coth\pi k\beta\end{array}\right\}$$

From rough graphs of these functions it is apparent that $u^2<1$ in the immediate vicinity of energies for which $k_1\alpha=1/2,\ 1,\ 3/2,\ \ldots$ which are just the positions of the energy levels allowed by the perturbation method, as they are the levels for a single valley with width α and infinitely high walls. It is difficult to give an estimate of the widths of these bands, but it is clear from the graph that they are very narrow when V_1 is large and k_1 small, approximately coinciding with the discrete levels for a single valley.

Real Crystals

In order to apply this method to real crystals, it is necessary to improve the starting point by considering a potential function similar to that shown in Fig. 2.

When $W>V_0$ the results are quite unchanged, the reflection regions being determined by the Bragg condition as previously discussed. All energy values are allowed even in the case of a semi-infinite lattice.

When $W<V_0$ some additions must be made to the previous results. The concepts of reflection and transmission being no longer applicable, one must make a study of the characteristic function itself, or what is the same thing, of the coefficients $(a_p,\ b_p)$. There is now the possibility that as $n\to\infty$, the modulus of the wave function will not remain bounded, so that certain ener-

[11] It can be verified from (8) that the real and imaginary parts of c_1 are still given by (13) when k_2 is pure imaginary.

gies may need to be excluded. Even for a finite lattice certain energy ranges will be excluded due to the circumstance that for any value of n, the boundary conditions at the edges of the lattice and (22) must be simultaneously satisfied; while for the semi-infinite lattice one must insure in addition the finiteness of the wave function. Probably the standing wave method described

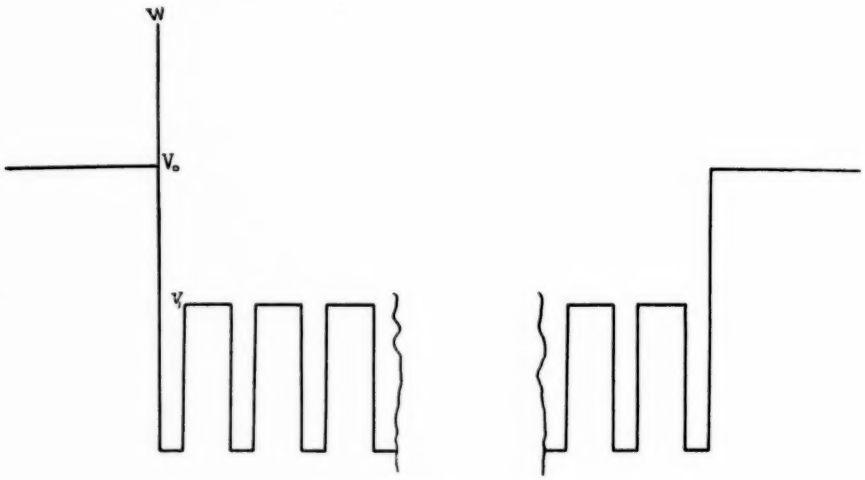

Fig. 2.

previously will still be applicable, although it seems possible that there may be additional excluded energies not appearing in such an analysis. This question would need to be studied in greater detail before the method of the present paper could be applied to metallic conduction problems.

Note added in proof: Kronig and Penney, Proc. Roy. Soc. **A130,** 499 (1931) have just published a treatment of the *infinite* lattice of the type shown in our Fig. 1 using functions of the type (28). The results are similar to these found here. The author intends to study in greater detail the connection of our general solution with this more special method since it seems possible that the use of a single function of the type (28) is associated with assumptions of periodic properties of ψ which are not altogether required by the nature of the problem.

HYPERFINE STRUCTURE AS A TEST OF A LINEAR WAVE EQUATION IN THE TWO-BODY PROBLEM

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(Received February 21, 1931)

Abstract

The proper treatment of the two-body problem is not known. Dirac's relativistic considerations, so successful in the problem of one electron, have been applied by Breit to the two-electron problem. Energy terms appear of which the physical reality is very doubtful. Here a very similar application is made to the problem of a nucleus and an electron, because of the failure of previous treatments of this problem to agree with measurements of hyperfine structure. The doubtful terms do not bring about agreement, so their reality remains improbable. The present state of the theory suggests that the proper interactions have not yet been introduced in the problem of hyperfine structure.

Introduction

DIRAC has satisfied the demands of relativity for the problem of one charged particle in a force field, obtaining spin as a consequence. Breit[1] has treated the problem of two bodies in a similar manner. He has improved the calculations of Gaunt[2] on the same subject by including the classical effects of retardation of potentials, as given by Darwin. A straightforward reduction of the linear equation, involving good approximations, leads to an equation for the largest components of the wave function. This may be compared directly with the wave equation resulting from a treatment of the atomic model with spins by the usual wave mechanical perturbation theory.[3] Breit's equation contains terms representing spin-orbit interactions (with factors in agreement with the relativistically correct results of Dirac and of Thomas and Frenkel for single electrons), terms expressing the magnetic spin-spin and orbit-orbit interactions, terms due to relativistic change of mass, terms appering in Dirac's results and having a meaning only for s-states, and in addition unexpected terms containing e^4 and no h as factors, which contradict the correspondence principle. One of these terms in e^4 Breit has tested[4] by calculating its probable effect on the He triplet. The results do not agree with experiment, whereas without this one term the agreement is quite as good as could be expected, considering the approximate nature of the wave functions involved. This contradiction means that the term making the disagreement, and perhaps all the terms in e^4, have no physical meaning. It is still barely possible that that invalidation may not be final, and even that the doubtful terms have a different meaning for a nucleus and an electron than for two

[1] G. Breit, Phys. Rev. **34**, 553 (1929).
[2] A. Gaunt, Proc. Roy. Soc. **A122**, 512 (1928); Trans. Roy. Soc. **228**, 151 (1929).
[3] W. Heisenberg, Zeits. f. Physik **49**, 499 (1926).
[4] G. Breit, Phys. Rev. **36**, 383 (1930).

electrons. The importance of the problem nurtures the hope that the following test of two of the terms in e^4 may be helpful, after the appearance of more copious data.

1. Consider an electron and a nucleus moving under one another's influence. No assumption is made regarding the spin of either. This differs from the helium problem in the absence of the field of the fixed nucleus and in the metamorphosis of one of the electrons into a nucleus. The Darwin-Hamiltonian will be,

$$H = p_{\mathrm{I}}^2/2m_{\mathrm{I}} + p_{\mathrm{II}}^2/2m_{\mathrm{II}} - p_{\mathrm{I}}^4/8c^2m_{\mathrm{I}}^3 - p_{\mathrm{II}}^4/8c^2m_{\mathrm{II}}^3 + e_{\mathrm{I}}e_{\mathrm{II}}/r - (e_{\mathrm{I}}e_{\mathrm{II}}/2c^2m_{\mathrm{I}}m_{\mathrm{II}})[(\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{p}_{\mathrm{II}})r + (\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{r})(\boldsymbol{p}_{\mathrm{II}}\cdot\boldsymbol{r})/r^3]. \quad (1)$$

Here the numeral I refers to the nucleus, II to the electron; $e_{\mathrm{I}} = Ze$, $e_{\mathrm{II}} = -e$; and $\boldsymbol{r}$ is a vector from the nucleus to the electron. This leads one to the equivalent of Breit's Eq. (6),

$$\Big(p_0 + \sum_{k=1,2,3}(\alpha_k^{\mathrm{I}}p_k^{\mathrm{I}} + \alpha_k^{\mathrm{II}}p_k^{\mathrm{II}}) + \alpha_4^{\mathrm{I}}m_{\mathrm{I}}c + \alpha_4^{\mathrm{II}}m_{\mathrm{II}}c + (e_{\mathrm{I}}e_{\mathrm{II}}/2c)\Big\{\sum_{k=1,2,3}\alpha_k^{\mathrm{I}}\alpha_k^{\mathrm{II}}r^{-1} + (\alpha^{\mathrm{I}}\cdot\boldsymbol{r})(\alpha^{\mathrm{II}}\cdot\boldsymbol{r})r^{-3}\Big\}\Big)\psi = 0 \quad (2)$$

with

$$p_0 = -\frac{h}{2\pi i}\frac{\partial}{c\partial t} - \frac{e_{\mathrm{I}}e_{\mathrm{II}}}{cr}; \quad p_k^{\mathrm{I}} = \frac{h}{2\pi i}\frac{\partial}{\partial x_k^{\mathrm{I}}}.$$

Here we have omitted entirely the four-potential A. The reduction of this equation will be identical with the calculation of Breit, and will lead to the following modification of his Eq. (48′):

$$\{E - (m_{\mathrm{I}} + m_{\mathrm{II}})c^2 - e_{\mathrm{I}}e_{\mathrm{II}}/r - p_{\mathrm{I}}^2/2m_{\mathrm{I}} - p_{\mathrm{II}}^2/2m_{\mathrm{II}} \quad (3.0)$$

$$+ p_{\mathrm{I}}^4/8m_{\mathrm{I}}^3c^2 + p_{\mathrm{II}}^4/8m_{\mathrm{II}}^3c^2 \quad (3.1)$$

$$+ (e_{\mathrm{I}}e_{\mathrm{II}}/2m_{\mathrm{I}}m_{\mathrm{II}}c^2)[(\boldsymbol{p}_{\mathrm{I}}\cdot\boldsymbol{p}_{\mathrm{II}})r^{-1} + \sum_{i,j}r^{-3}(x_i^{\mathrm{II}} - x_i^{\mathrm{I}})(x_j^{\mathrm{II}} - x_j^{\mathrm{I}})p_i^{\mathrm{I}}p_j^{\mathrm{II}}] \quad (3.2)$$

$$- (e_{\mathrm{I}}e_{\mathrm{II}}hi/8\pi c^2)r^{-3}(\boldsymbol{r}\cdot[\boldsymbol{p}^{\mathrm{I}}m_{\mathrm{I}}^{-2} - \boldsymbol{p}^{\mathrm{II}}m_{\mathrm{II}}^{-2}]) \quad (3.3)$$

$$+ (e_{\mathrm{I}}e_{\mathrm{II}}h/8\pi c^2)r^{-3}(-m_{\mathrm{I}}^{-2}[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{I}}]\cdot\sigma^{\mathrm{I}} + m_{\mathrm{II}}^{-2}[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{II}}]\cdot\sigma^{\mathrm{II}} \quad (3.4)$$

$$+ (2/m_{\mathrm{I}}m_{\mathrm{II}})\{-[\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{II}}]\cdot\sigma^{\mathrm{I}} + [\boldsymbol{r}\times\boldsymbol{p}^{\mathrm{I}}]\cdot\sigma^{\mathrm{II}}\}) \quad (3.5)$$

$$- (e_{\mathrm{I}}e_{\mathrm{II}}/m_{\mathrm{I}}m_{\mathrm{II}})(h/4\pi c)^2\langle(\nabla^{\mathrm{II}}\cdot\sigma^{\mathrm{I}})(\nabla^{\mathrm{I}}\cdot\sigma^{\mathrm{II}})r^{-1}\rangle \quad (3.6)$$

$$- (e_{\mathrm{I}}^2e_{\mathrm{II}}^2/4(m_{\mathrm{I}}+m_{\mathrm{II}})c^2)[3r^{-2} - 2(\sigma^{\mathrm{I}}\cdot\sigma^{\mathrm{II}})r^{-2} + (\sigma^{\mathrm{I}}\cdot\boldsymbol{r})(\sigma^{\mathrm{II}}\cdot\boldsymbol{r})r^{-4}]\}\psi_{a,b} = 0 \quad (3.7)$$

For the sake of easy comparison, the energy equation which will be derived in §2 from this wave equation is entered here.

$$E = E_1 + E_2$$

E_1 is the same for all the states in which we are interested and consists of the unperturbed energy augmented by the contributions of (3.1), (3.2), and (3.3). E_2 splits up the doublet and is given by

$$-E_2 = (h^2e_Ie_{II}/8\pi^2c^2)\overline{r^{-3}}[m_I^{-2}(\overline{\boldsymbol{l}\cdot\mathbf{s}^I}) + m_{II}^{-2}(\boldsymbol{l}\cdot\mathbf{s}^{II}) \tag{4.4}$$

$$- (2/m_Im_{II})\{(\overline{\boldsymbol{l}\cdot\mathbf{s}^I}) + (\boldsymbol{l}\cdot\mathbf{s}^{II})\}] \tag{4.5}$$

$$- (e_Ie_{II}/m_Im_{II})(h/2\pi c)^2\overline{r^{-3}}\,[(\overline{\mathbf{s}^I\cdot\mathbf{s}^{II}}) - 3\overline{(\mathbf{s}^I\cdot\boldsymbol{r})(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}} \tag{4.6}$$

$$+ (e_I^2e_{II}^2/(m_I + m_{II})c^2)\overline{r^{-2}}\,[(\overline{\mathbf{s}^I\cdot\mathbf{s}^{II}}) - \overline{(\mathbf{s}^I\cdot\boldsymbol{r})(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}}] \tag{4.7}$$

(3.4) (and also (4.4)) represent the interaction of each spin with the field due to its own orbital motion, while (3.5) gives the interaction of the spin of each particle with the orbit of the other. (3.6) corresponds to the classical interaction energy of two dipoles. (3.7) contains the doubtful terms in e^4. If physically extant, only the last of the three terms would effect the helium triplet separation, so it alone was tested by Breit. Each of the last two terms would effect hyperfine structure, so we can test them both. The first gives only a displacement common to all the levels.

2. In the perturbation problem, (3) is the perturbed wave equation. To determine the unperturbed wave functions, we consider all the terms beyond (3.0) as perturbation terms, so that (3.0) becomes the unperturbed equation. The coordinates are taken to be those in which the center of gravity is at rest, since a transformation can always be made from more general coordinates of two particles to the coordinates of the center of gravity and the relative coordinates of the particles. The translation of the center of gravity being separated from the problem, $\boldsymbol{p}^I = -\boldsymbol{p}^{II}$. Thus we have the hydrogen wave equation, and hence use hydrogenic wave functions. The wave function in the unperturbed equation, as in (3), has two indices, each of which may have two values. The first index refers to the nuclear spin orientation, and is operated upon by σ^I; the second to the spin of the electron, and is acted upon by σ^{II}. As a function of space and spin coordinates, the unperturbed function is separable,

$$\psi_{a,b}(r, \theta, \phi) = S_a{}^IS_b{}^{II}u(r, \theta, \phi)$$

where a and b may each be either α or β of Pauli's theory, and σ^I and σ^{II} operate on S^I and S^{II}, respectively, in the usual manner. $S^{II}u$ might be replaced by the one-electron wave function stabilized for spin-orbit interaction, such as given by Bartlett,[5] e.g., and the resulting ψ would give the diagonal terms of an energy matrix from which hyperfine splitting could be had by sum rules. Since the wave function is separable in radial and angular parts, we may obtain the result of the angular integrations by considering the operators as vectors in the vector model, and averaging over the precessions. $[\boldsymbol{r}\times\boldsymbol{p}^I] = -[\boldsymbol{r}\times\boldsymbol{p}^{II}]$ is the orbital angular momentum operator. Since Breit has used in effect the negative of the Pauli matrices, σ becomes $-2\mathbf{s}$, where $|s| = \frac{1}{2}$. These substitutions in (3) give (4). In reducing it to an expression in the quantum numbers, Landé cosines are used. Goudsmit[6] has explained in detail a method for obtaining $\overline{(\mathbf{s}^I\cdot\boldsymbol{r})\,(\mathbf{s}^{II}\cdot\boldsymbol{r})r^{-2}}$. It consists essentially in making angular integrations in the case of a strong field, when the quantum vectors

[5] J. H. Bartlett, Jr., Phys. Rev. **35**, 230 (1930).

[6] S. Goudsmit, Phys. Rev. **37**, 663 (1931).

are decoupled, and using the results to find the value of the interaction without field by means of energy sum rules.

From the latter term of (4.4) (the other term in $(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}})$ is negligible) we get the energy that gives rise to the doublet separation:

$$E' = -(h^2e_{\mathrm{I}}e_{\mathrm{II}}/8\pi^2c^2m_{\mathrm{II}}{}^2)\overline{r^{-3}}(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}})$$
$$= A'(\boldsymbol{l}\cdot\mathbf{s}^{\mathrm{II}}) = A'\tfrac{1}{2}\{j(j+1) - l(l+1) - \tfrac{3}{4}\} \quad (5)$$

It is apparent in (4) that the hyperfine structure contains the same constant A' which is determined empirically by the doublet separation. The following expressions, which give the splitting up of the two doublet levels, are derived from (4.4), (4.5), and (4.6). The order of the terms has been preserved.

$$E''_j = A_j''(\mathbf{s}^{\mathrm{I}}\cdot j) = A_j''\tfrac{1}{2}\{f(f+1) - j(j+1) - s^{\mathrm{I}}(s^{\mathrm{I}}+1)\} \quad (6)$$

$$A''_{l+\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left[\frac{2l}{l+\frac{1}{2}} - \frac{1}{l+\frac{1}{2}} + \frac{3}{(2l+3)(l+\frac{1}{2})} + \delta\frac{8\pi^2e_{\mathrm{I}}e_{\mathrm{II}}m_{\mathrm{II}}}{h^2}\frac{\overline{r^{-2}}}{\overline{r^{-3}}}\left\{\frac{1}{l+\frac{1}{2}} - \frac{2}{(2l+3)(l+\frac{1}{2})}\right\}\right] \quad (7)$$

$$A''_{l-\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left[2\frac{l+1}{l+\frac{1}{2}} + \frac{1}{l+\frac{1}{2}} + \frac{3}{2(l-\frac{1}{2})(l+\frac{1}{2})} - \delta\frac{8\pi^2e_{\mathrm{I}}e_{\mathrm{II}}m_{\mathrm{II}}}{h^2}\frac{\overline{r^{-2}}}{\overline{r^{-3}}}\left\{\frac{1}{l+\frac{1}{2}} + \frac{1}{(l-\frac{1}{2})(l+\frac{1}{2})}\right\}\right]. \quad (8)$$

The symbol δ has the value unity of the terms in e^4 are physical, otherwise it is zero.

3. To compare the terms we must have an idea of the ratio of the radial integrals. For a Coulomb field,

$$\overline{r^{-2}} = \frac{Z^2}{n^3(l+\frac{1}{2})}\frac{1}{a_0{}^2}, \quad \overline{r^{-3}} = \frac{Z^3}{n^3l(l+\frac{1}{2})(l+1)}\frac{1}{a_0{}^3}, \quad a_0 = \frac{h^2}{4\pi^2m_{\mathrm{II}}e^2}. \quad (9)$$

For the heavy elements some sort of approximation must be used. The electron cloud alters the radial part of the wave function by producing a non-coulomb interaction. We will content ourselves with the classical application of the charged shell model of the atom, as used by Landé for doublet separations.[7] Using (9) for outer and inner orbital segments, we get

$$\overline{r^{-2}} = \frac{2Z_0{}^2}{n_0{}^3(l+\frac{1}{2})}\frac{1}{a_0{}^2}, \qquad \overline{r^{-3}} = \frac{Z_iZ_0{}^2}{n_0{}^3l(l+\frac{1}{2})(l+1)}\frac{1}{a_0{}^3}$$

of which the ratio is

$$\overline{r^{-2}}/\overline{r^{-3}} \approx 2l(l+1)a_0/Z.$$

This in (7) and (8) gives

$$A''_{l+\frac{1}{2}} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left\{\frac{2l(l+1)}{(l+\frac{1}{2})(l+\frac{3}{2})} - \delta\frac{8l(l+1)}{2l+3}\right\} = \frac{m_{\mathrm{II}}}{m_{\mathrm{I}}}A'\left\{\frac{16}{15} - \delta\frac{16}{5}\right\}$$

[7] A. Landé, Zeits. f. Physik **25**, 46 (1924).

$$A''_{l-\frac{1}{2}} = \frac{m_{II}}{m_I} A' \left\{ \frac{2l(l+1)}{(l-\frac{1}{2})(l+\frac{1}{2})} + \delta \frac{4l(l+1)}{l-\frac{1}{2}} \right\} = \frac{m_{II}}{m_I} A' \left\{ \frac{16}{3} + \delta 8 \right\}.$$

The last members are for the case $l=1$. The presence of other electrons also replaces $\overline{Zr^{-3}}$ by $\overline{Z_{eff} r^{-3}}$ in the expression for A', but the numerical change is small enough that it need not interest us here.[8]

The present treatment leads naturally to a nuclear spin with but two orientations possible and a Landé g-factor 2 in units $e_I h/4\pi m_I c$. For the terms that classically have a meaning it is easy to believe that we may extend the result to other cases with the vector model by assuming a larger nuclear spin vector s^I in (6), selecting its value and a different value of g to accord with observed intervals or intensity ratios. We postulate tentatively that a similar treatment of the terms in e^4 will give an estimate of their contribution to the energies.

A comparison is made with the few experimental data available,[9] which are for ^2P. In Tl the nuclear moment is $\frac{1}{2}$ but in Bi it is $4\frac{1}{2}$.

TABLE I.

	A' exp.	A'' exp.	A'' calc. $\delta=0$	A'' calc. $\delta=1$	A'' exp.	A'' calc. $\delta=0$	A'' calc. $\delta=1$
Tl I*	5195 cm^{-1}	0.72	0.074	0.18	~0.02	0.015	−0.03
*Bi***	10000	0.40	0.14	0.35	~0.02	0.03	−0.06

* John Wulff, appearing in Zeits. f. Physik, communicated to Professor Goudsmit.
** Indirectly derived from Bi I and II data. R. A. Fisher and S. Goudsmit, Phys. Rev., in print.

The classical values, with $\delta=0$, do not agree with experiment even when multiplied by the arbitrary factor $g(I)$ which the usual theory allows. When such an arbitrary factor is introduced, the agreement in the case $\delta=1$ is even worse. However, the present treatment of the problem, when not extended hypothetically, does not permit of such a factor. For the large separations, of which the measurements are most certain, the agreement is better with $\delta=1$ than with $\delta=0$.

In the classical terms the value of the nuclear magnetic moment is definitely determined as Zm_{II}/m_I Bohr magnetons for the nuclear spin $\frac{1}{2}$. This is as assumed and discussed by Jackson[9] and by Fermi[8].

This paper stresses once more the fact that we have at present no satisfactory theory of spin-spin interaction.

I thank Professor Uhlenbeck and Professor Goudsmit for very helpful suggestions.

[8] E. Fermi, Zeits. f. Physik **60**, 332 (1930).

[9] The results for In I by Jackson (Proc. Roy. Soc. **A128**, 508, 1930) and by McLennan and Allin (Proc. Roy. Soc. **A129**, 208, 1930) disagree too radically to be of use at present. In Bi III and Tl III the second member of the P series is known, but second order effects make the values of A_i'' for our purpose uncertain. (Vide H. Casmir, Phys. Rev., in print.)

ABSORPTION BANDS OF HYDROGEN CYANIDE GAS IN THE NEAR INFRARED

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Abstract

The absorption spectrum of gaseous hydrogen cyanide has been investigated by photographic methods in the region λ7000–9200. Two weak bands of very simple structure were found, having P and R branches but no Q branches. The band at λ7912 is apparently a harmonic of a fundamental band at 3.04μ, and the very weak band at λ8563 is a combination band. The hydrogen cyanide molecule is linear in the normal state, and has a moment of inertia $I=18.79\times10^{-40}$ g·cm². The distance of separation of the carbon and nitrogen atoms is estimated to be 1.15×10^{-8} cm. Hydrogen cyanide is discussed in regard to its three fundamental oscillations which have frequencies 3290, 2090, and 710, respectively, and in regard to its dissociation energy and dissociation products. The evidence requires a molecular structure represented by the formula HCN, and shows that the normal molecule is built from a normal hydrogen atom and a normal CN radical. The absorption of cyanogen gas has also been investigated in the photographic infrared, but no absorption bands could be detected.

Introduction

HYDROGEN cyanide has been the subject of two previous infrared investigations. W. Burmeister[1] observed two double bands with maxima at 14.33μ and 13.60μ, and at 7.22μ and 6.95μ, respectively, a single strong maximum at 3.04μ, and doubtful bands at 4.8μ and 3.6μ. E. F. Barker,[2] working with greater dispersion, confirmed the doubtful bands and found for the one three maxima at 4.79, 4.756, and 4.723μ, and in the case of the other apparently a strong Q branch with maximum at 3.564μ and two weak maxima on either side. Slight evidence of a rotational structure was found in the band at 7μ.

A calculation of the moment of inertia of the hydrogen cyanide molecule from the separation of the maxima of the double band at 14μ, with the use of a classical formula, yielded the improbably large value $I=33\times10^{-40}$.[3] The separation of the maxima in the band at 7μ is much greater and has been interpreted as due to rotation about an axis with moment of inertia $I=0.907\times10^{-40}$.[4]

Experimental Procedure

The hydrogen cyanide gas used in the investigation was prepared by dropping a concentrated solution of sodium cyanide into sulphuric acid. The gas

[1] W. Burmeister, Verh. d. D. Phys. Ges. **15**, 589 (1913).
[2] E. F. Barker, Phys. Rev. **23**, 200 (1924).
[3] R. C. Tolman and R. M. Badger, Jour. Amer. Chem. Soc. **45**, 2277 (1923).
[4] Schaefer and Matossi, Das Ultrarote Spectrum, Berlin, 1930.

evolved was dried with calcium chloride and then condensed in a tube immersed in a freezing mixture. This tube was then connected to the evacuated absorption cell until equilibrium between liquid and vapor was established at room temperature. The gas pressure in the cell was consequently usually slightly less than one atmosphere. It seemed undesirable to attempt to increase the pressure by warming the apparatus, since even at atmospheric pressure the absorption lines were rather broad.

The absorption cell was a steel tube 280 cm in length, with a mirror at one end so that the light from the tungsten lamp source traversed it twice. The exposures were taken with the first order of a ten-foot grating in an Eagle mounting, using Eastman Infrared Sensitive Plates hypersensitized in ammonia. As calibration spectrum the iron lines in the second order were used.

Since both absorption bands were very weak it was not possible to make direct measurements on the plates with the use of a comparator. Microphotometer records were consequently made of absorption and comparison spectra, side by side on the same plates, using a linear enlargement of ten times. The tabulated wave-lengths, except for a few weak lines, were calculated from the mean of measurements made on four photometer curves obtained from different parts of two spectral plates.

Experimental Results

A careful examination of spectrograms covering the region λ7000–9200 resulted in the discovery of two similar absorption bands at λ7912 and λ8563, respectively. Both are weak, the latter extremely so, and the lines are broad as is to be expected in a saturated vapor. Each band has a P and an R branch, a missing zero line, and no apparent Q branch. The convergence in the R branches is so large that at first sight the bands appear to have a head. Due to the weakness of the absorption no attempt has been made to estimate relative intensities. The two branches have in each case about equal intensity, and as should be expected there is no indication of alternating intensities.

The wave-lengths and corresponding frequencies on the lines measured are recorded in the accompanying tables. A single question mark indicates low probable accuracy of measurement, and a double question mark, possible doubt as to the reality of the line. The measurements of the lines in the R branches are probably the less reliable due to incomplete resolution of the rather broad lines.

It should be mentioned that cyanogen gas was also studied in the course of this investigation, with pressures up to three atmospheres, but no absorption could be detected.

Discussion of the Results

The rotational energy levels of the upper and lower vibrational states of the molecule were isolated by means of the usual combination relations:

$$\Delta_2 F'(J) = R(J) - P(J) = F'(J+1) - F'(J-1) \sim 4B'(J+\tfrac{1}{2})$$

$$\Delta_2 F''(J) = R(J-1) - P(J+1) = F''(J+1) - F''(J-1) \sim 4B''(J+\tfrac{1}{2}).$$

TABLE I. *The HCN band at λ7912.*

	R-Branch		*P*-Branch					
J	λ	ν	λ	ν	$\Delta_2F''(J)$	$\frac{\Delta_2F''(J)}{J+1/2}$	$\Delta_2F'(J)$	$\frac{\Delta_2F'(J)}{J+1/2}$
0	7910.4	12638.1						
1	08.3	41.5	7913.8	12632.7	8.1	5.39	8.8	5.87
2	06.5	44.4	15.5	30.0	14.6	5.84	14.4	5.76
3	04.9	46.9	17.4	26.9	20.8	5.94	20.0	5.71
4	03.3	49.5	19.5	23.6	27.0	6.00	25.9	5.76
5	01.8	51.9	21.8	19.9	32.8	5.96	32.0	5.82
6	00.4	54.1	23.8	16.7	38.5	5.92	37.4	5.76
7	7898.9	56.5	25.9	13.4	44.0	5.87	43.1	5.74
8	97.7	58.4	28.0	10.1	50.3	5.92	48.3	5.68
9	96.4	60.5	30.4	06.2	55.8	5.87	54.3	5.73
10	95.5	62.0	32.7	02.6	61.9	5.89	59.4	5.65
11	94.0	64.4	35.2	12598.6	67.0	5.82	65.8	5.73
12	92.9	66.1	37.5	95.0	73.6	5.88	71.1	5.69
13	91.9	67.7	40.1	90.8	79.4	5.88	76.9	5.70
14	90.8	69.5	42.7	86.7	85.3	5.88	82.8	5.71
15	90.0	70.8	45.4	82.4	91.2	5.88	88.4	5.70
16	88.8	72.7	48.0	78.3	97.0	5.88	94.4	5.72
17	88.1	73.8	50.8	73.8	103.2	5.90	100.0	5.72
18			53.6	69.5	108.6	5.87		
19			56.3	65.2				
20			59.7	59.8				
21			62.4	55.6				
22			65.4(?)	50.8				
23			68.6(?)	45.8				
24			71.8(?)	40.8				
25			75.2(?)	35.4				
26			78.0(?)	31.0				
27			81.8(?)	25.1				

TABLE II. *The HCN band at λ8563.*

	R-Branch		*P*-Branch					
J	λ	ν	λ	ν	$\Delta_2F''(J)$	$\frac{\Delta_2F''(J)}{J+1/2}$	$\Delta_2F'(J)$	$\frac{\Delta_2F'(J)}{J+1/2}$
0	8561.5(?)	11677.0						
1	59.3	80.0	8565.4(??)	11671.7	8.9	5.92	8.3	5.53
2	57.2	82.8	68.0	68.1	14.7	5.89	14.7	5.88
3	55.4	85.4	70.1	65.3	20.6	5.89	20.1	5.74
4	53.3	88.2	72.3	62.2	26.6	5.94	26.0	5.77
5	51.7	90.4	74.9	58.7	33.0	6.00	31.7	5.76
6	50.1	92.6	77.5	55.2	38.3	5.89	37.4	5.76
7	48.2	95.2	79.8	52.1	44.3	5.91	43.1	5.74
8	46.6	97.3	82.6	48.3	50.3	5.91	49.0	5.76
9	45.1	99.4	85.1	44.9	56.3	5.92	54.5	5.74
10	43.6(?)	11701.6	88.0	41.0	62.0	5.90	60.5	5.77
11	42.1(?)	03.5	90.6	37.4	68.0	5.92	66.1	5.75
12	40.8(?)	05.3	93.5	33.5	73.9	5.92	71.8	5.74
13	39.5(?)	07.1	96.4	29.6	80.3	5.94	77.5	5.74
14			99.8	25.0	86.0	5.94		
15			8602.7	21.1				
16			05.3	17.4				
17			08.8	12.8				
18			11.7	08.9				
19			15.1	04.3				

These differences are presented in the right side of Tables I and II. No effect of the stretching of the molecule as a result of rotation could be detected, and within the accuracy of measurement the rotational energies in all three vibrational states may be represented by simple formulas of the form:

$$E_{\text{rot}} = J(J+1)B.$$

The best values for the constants for the two bands are given in Table III. The differences in vibrational energies of upper and lower states, and the

TABLE III. *Constants of the HCN bands at λ7912 and λ8563.*

λ	ν_0	B''	$B'-B''$	I''
7911.9	12635.8	1.472	−0.044	18.79×10^{-40}
8563.3	11674.5	1.480	−0.042	18.69×10^{-40}

difference in the rotational energy constants, $B'-B''$, were obtained from a graphical treatment of the combinations:

$$\tfrac{1}{2}[R(J)+P(J+1)] = \nu_0 + (J+1)^2(B'-B'').$$

The slight difference in the value of B'', the rotational constant for the ground state, as determined from the two bands, is probably not greater than experimental error as the two bands seem to have a common lower level. The value determined from the data on the band at λ7912 is probably the more accurate.

STRUCTURE OF THE HYDROGEN CYANIDE MOLECULE

The simplicity of the two bands here investigated leaves no doubt as to the linearity of the hydrogen cyanide molecule in its normal state, and also in the two other vibrational states concerned. It still remains to be discussed which of the three possible arrangements of the three atoms in a straight line is the correct one. The arrangement with the hydrogen in the center is at once ruled out by the relatively small moment of inertia, ($I=18.79\times10^{-40}$) and need not be discussed on the grounds of chemical improbability. Whether the gas known to chemists should be designated as hydrogen cyanide, HCN, or iso-cyanide, HNC, or whether it may be a mixture of two molecular species has been the subject of numerous discussions, and it seems to be worth while to consider what the spectroscopic evidence has to say in this regard.

We will simply mention at this point that the relation of all the observed infrared bands is such that they are apparently due to only one type of molecule. Further, their intensity is so great that this molecular species must constitute by far the greater part of hydrogen cyanide gas. This particular molecule will be the one with which we shall be concerned, and from now on we shall speak of it as the hydrogen cyanide molecule, and shall examine the data with the purpose of determining its structure. We shall now proceed to discuss three pieces of information which are derived from spectral data, namely the moment of inertia of the molecule, the frequencies of vibration, and the heat of dissociation.

The moment of inertia of the hydrogen cyanide molecule in the normal state, as determined from the data on the band at λ7912 is, $I = 18.79 \times 10^{-40}$ g·cm². The fact that this constant is about half as large as that previously estimated from the doublet separation of the band at 14μ may possibly be accounted for by the low resolution used in studying this latter band. It is of course not possible to determine uniquely both interatomic distances in the molecule from the moment of inertia alone. However, the moment of inertia is not very sensitive to the position of the light hydrogen atom, and an estimate of the carbon-nitrogen separation may be made. In Fig. 1 is plotted

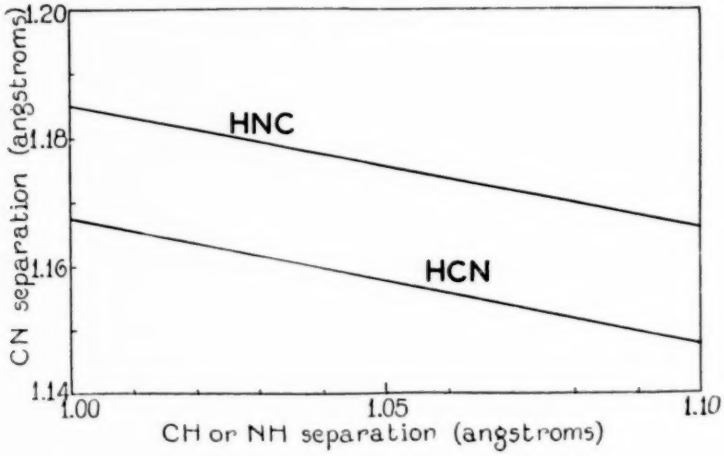

Fig. 1. The C-N separation plotted as a function of the C-H, or N-H separation for HCN and HNC molecular models with $I = 18.79 \times 10^{-40}$.

this distance as a function of the H-C separation, assuming the structure HCN, and of the H-N separation for the HNC structure, with the given moment of inertia. In either case the distance is small and strongly suggests a triple bond linkage between carbon and nitrogen. We may compare with the internuclear separation in the normal state of the CN radical, 1.17×10^{-8} cm.

Modes of Oscillation of the Hydrogen Cyanide Molecule

The observed hydrogen cyanide bands may all be fitted into one simple scheme as given in Table IV, requiring three fundamental frequencies.

Table IV. *Designation of the HCN bands.*
$\nu_1 = 3333.7\ v - 43.7\ v^2$; $\nu_2 = 2090$; $\delta = 710$

Band	ν(cm^{-1})	Designation
14μ	710	δ
7μ	1411	2δ
4.7μ	2090 (approx)	ν_2
	2112	3δ
3.6μ	2805	$\nu_2+\delta$ (and possibly 4δ)
3.04μ	3290	ν_1
0.8563μ	11675	$3\nu_1+\nu_2$
0.7912μ	12636	$4\nu_1$

The designation of the strong band at 3.04μ as a fundamental, and the band at λ7912 as one of its harmonics seems without objection. These two bands are represented within experimental error by the formula $\nu = 3333.7\, v - 43.7\, v^2$. That the bands at 14μ and 7μ are fundamental and first harmonic of a "deformation" oscillation is also reasonable, as such an oscillation should be expected to have a low frequency. A deformation oscillation does not necessarily lead to the presence of a strong Q branch as has been shown in the case of acetylene.[5] The choice of the other fundamental frequency, which seems to be comparatively inactive, is more difficult. The form of the unresolved band at 4.7μ suggests the overlapping of two bands, one of which is probably the fundamental in question and the other a harmonic of the 14μ band. The choice of a frequency around 2100 is confirmed by the combination band at λ8563, and seems settled by recent work on the Raman spectrum of liquid hydrogen cyanide.[6]

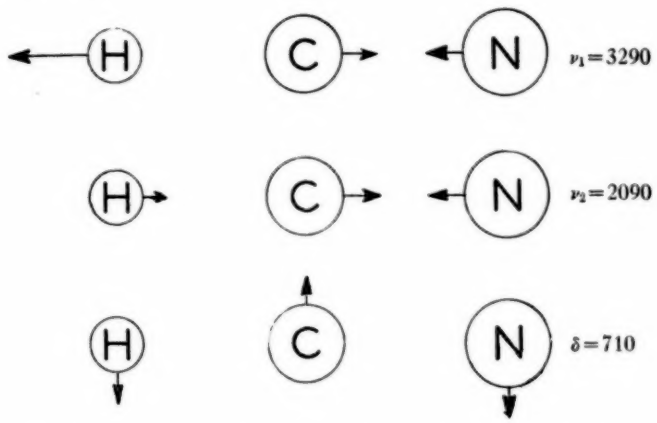

Fig. 2. The fundamental modes of oscillation of the HCN molecular model.

If we represent the hydrogen cyanide molecule by a mechanical model with three masses in the ratio 1.008:12:14, bound by Hooke's law forces, and arranged in a straight line, we find that this model does in fact have three fundamental modes of vibration, all of which will be "active," so to speak. Two of these may be designated as "valence" oscillations, the third as a "deformation" oscillation, as seen in Fig. 2. (Cf. the discussion of molecular oscillation by Mecke.[5]) By the application of normal coordinate methods it is possible to evaluate the ratio of the "valence" force constants which is required to fit the observed frequencies ν_1 and ν_2. That is we may estimate the ratio k_1/k_2 of the constants of the restoring forces which tend to maintain the equilibrium separation between carbon and nitrogen, and between hydrogen and the atom to which it is linked. Since the carbon and nitrogen atoms are of nearly equal mass it does not matter very much which of the two possible

[5] R. Mecke, Zeits. f. Physik, **64,** 173 (1930).
[6] Dadieu and Kohlrausch, Berichte **63,** 1657 (1930).

molecular models is considered. For the HCN arrangement we find $k_1/k_2 = 3.2$ and for HNC nearly the same value, 3.1. The former is nearly exactly the ratio of the force constants for CN in the normal state, and for HCl (or CH), and whichever model we choose is strong evidence for a triple bond between carbon and nitrogen. The ratio would be approximately 2 for a double bonded structure, as can for example be seen from a comparison of the binding constants in acetylene and ethylene.[5]

Dissocation Products and Dissociation Energy of Hydrogen Cyanide Molecule

We shall now consider the products of a dissociation process in which the hydrogen atom is removed from a hydrogen cyanide molecule. Three energy states of the CN radical are known. The normal state is a $^2\Sigma$ state formed from a ^4S nitrogen atom and a ^5S carbon atom.[7] A small internuclear separation and high oscillational frequency are evidence of a triple bond. The two excited states are formed from ^4S nitrogen and ^3P carbon. The lower of these, a $^2\Pi$ level with 1.8 volts excitation energy, has a relatively loose binding indicative of a double bond, but the higher, a $^2\Sigma$ state, has surprising rigidity considering its dissociation products and small dissociation energy.

The consideration of the oscillational frequencies rendered it improbable that the normal hydrogen cyanide molecule is formed from the CN radical in the $^2\Pi$ state, and this improbability is confirmed by the following energy considerations. The dissociation energy of normal hydrogen cyanide gas molecules into normal hydrogen atom and CN radical may be calculated from the data embodied in the following equations. These data are partly spectroscopic values, and partly thermal values corrected to the absolute zero by the use of specific heat data.

$$\tfrac{1}{2}H_2 + C(\text{graphite}) + \tfrac{1}{2}N_2 = \text{hydrogen cyanide} - 30{,}200 \text{ cals } (-1.31 \text{ volts}) \quad (1)$$

$$N_2 = 2N - 212{,}000 \text{ cals } (-9.2 \text{ volts}) \quad (2)$$

$$H_2 = 2H - 100{,}000 \text{ cals } (-4.34 \text{ volts}) \quad (3)$$

$$C(\text{graphite}) = C(\text{gas}) - 158{,}000 \text{ cals } (-6.86 \text{ volts})^8 \quad (4)$$

$$CN(\text{normal}) = C(\text{normal}) + N(\text{normal}) - 187{,}000 \text{ cals } (-8.1 \text{ volts})^7 \quad (5)$$

$$CN(\text{normal}) = CN(^2\Pi) - 41{,}500 \text{ cals } (-1.8 \text{ volts})^7 \quad (6)$$

From a combination of these data we find:

$$\text{hydrogen cyanide(normal)} = H(\text{normal}) + CN(^2\Pi) - 138{,}000 \text{ cals } (-6.0 \text{ volts}) \quad (7)$$

This is again strong evidence that normal hydrogen cyanide molecule is not directly formed from $^2\Pi$ CN radical, since an abnormally strong binding for the hydrogen would be required by Eq. (7). We should expect a molecule so built to be of the form HNC, and there seems to be no reason to suppose that the binding energy of hydrogen to nitrogen in this case should be much greater than the energy of the H-C linkage. We find for example that the

[7] W. Heitler and G. Herzberg, Zeits. f. Physik **53,** 52 (1929).
[8] Brody and Millner, Chem. Zent. I, 237 (1928).

dissociation energy of NH_3 into its atoms is about 4.0 volts per hydrogen atom. A similar argument renders it even less likely that hydrogen cyanide is formed from CN in a state of excitation higher than the $^2\Pi$ state.

We are then left with the one possibility that the dissociation products of normal hydrogen cyanide are a normal hydrogen atom and a normal CN radical. This seems to require the molecular structure HCN, and we may write:

$$\text{HCN(normal)} = \text{H(normal)} + \text{CN(normal)} - 97{,}000 \text{ cals } (-4.2 \text{ volts}) \quad (8)$$

This result is thoroughly reasonable and may be compared with the value $-100{,}000$ cals. (-4.34 volts) which is the dissociation energy of HCl molecule.

It is interesting to consider the possibility of the existence of a hydrogen iso-cyanide molecule formed from hydrogen atom and $^2\Pi$ CN radical. This molecule, as stated above, would probably have the form HNC but would be non-linear. If we may estimate the H-N binding energy at about 4.2 volts, HNC should have about 41,500 cals (1.8 volts) more energy then HCN. We may make a rough estimate of the relative amounts of the two forms in an equilibrium mixture if we assume that the two forms have about the same specific heat and the same entropy. We find

$$K_{298^\circ} = \frac{\text{HCN}}{\text{HNC}} = 10^{30} \text{ (approx)}.$$

We must then conclude that hydrogen cyanide gas consists almost entirely of linear molecules of the form HCN.

One may be tempted to calculate a dissociation energy for HCN by the use of the vibrational constants in the formula representing the bands with fundamental at 3.04μ. The value so obtained is 6.4 volts, but can not be very significant since only one band of the series has been accurately measured and the constants are consequently inexact. In any case linear extrapolations are found to give uncertain results even in the case of diatomic molecules, and with polyatomic molecules seem to give consistently too high values. This might in some cases be explained by saying that the dissociation leaves a radical in an excited electronic state, but in other cases this is improbable. There seems to the authors to be a certain difficulty in principle in calculating dissociation energies of polyatomic molecules from spectral data. When one of the fundamental oscillations of such a molecule is increased in amplitude until an atom splits off, at the moment of separation the radical remaining may very likely be in a distorted condition, and after the separation will continue to vibrate with considerable energy. This remaining vibrational energy must be subtracted from the value obtained from the band series extrapolation in order to obtain the true dissociation energy. We hope to discuss this question more in detail in a later paper, and have some experiments in progress which may clarify the situation.

THE IONIZATION OF MERCURY VAPOR BY ELECTRON IMPACT

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Abstract

Quantitative measurements have been made of the total number of positive charges per electron per centimeter path at a definite pressure and temperature in mercury vapor as a function of the energy of the impacting electrons out to 750 volts. The maximum efficiency 19.40 occurs at about 85 volts.

"*Ultra-ionization potentials*" were found at 10.60, 10.76, 10.88, 11.06, 11.27, 11.40, 11.55, 11.70, 11.78, 11.92, 12.00, 12.06, 12.17, 12.28, 12.40, 12.77, 13.55, 18.20, 19.36, 20.40, and 29.50 volts. Most of these agree with those previously observed.

A METHOD has recently been described[1] for measuring the total number of positive charges formed by electron impact in gases at low pressure. The results in helium, neon, and argon have been reported. The present paper gives a description of the results of a study of mercury vapor.

Compton and Van Voorhis,[2] T. J. Jones,[3] and Bleakney[4] measured the efficiency of ionization of mercury vapor by electron impact and obtained values which agree qualitatively. Lawrence,[5] and Hughes and Van Atta[6] have observed by indirect methods sharp increases, near the ionization potential, in the number of ions formed by electrons as their energy was increased. Haupt,[7] and Nielsen and Potter,[8] by more direct methods, also observed several of these critical potentials which Lawrence has called "ultra-ionization potentials."

The writer has redetermined the efficiency of ionization of mercury vapor and has observed a number of abrupt changes in the slope of the efficiency curves. The potentials at which these new modes of ionization set in agree quite well with those previously observed and several of the new ones found account for some of the apparent discrepancies between those found by Lawrence and by Hughes and Van Atta.

Apparatus and Procedure

The apparatus, Fig. 1, was constructed entirely of tantalum. The more essential parts were insulated with quartz. The metal parts were baked out at a yellow heat before they were sealed into the Pyrex tube.

[1] P. T. Smith, Phys. Rev. **36,** 1293 (1930).
[2] Compton and Van Voorhis, Phys. Rev. **27,** 724 (1926).
[3] T. J. Jones, Phys. Rev. **29,** 450 (1927).
[4] W. Bleakney, Phys. Rev. **34,** 157 (1929); **35,** 139 (1930).
[5] E. O. Lawrence, Phys. Rev. **28,** 947 (1926).
[6] A. L. Hughes and C. M. Van Atta, Phys. Rev. **36,** 214 (1930).
[7] C. R. Haupt, 167th Meeting of the American Physical Society.
[8] W. M. Nielsen, Phys. Rev. **37,** 87 (1931).

The filament, F, was a thin tungsten ribbon about 0.075 cm wide and placed within 1 mm of the hole, S_1, which was about 0.034 cm in diameter.

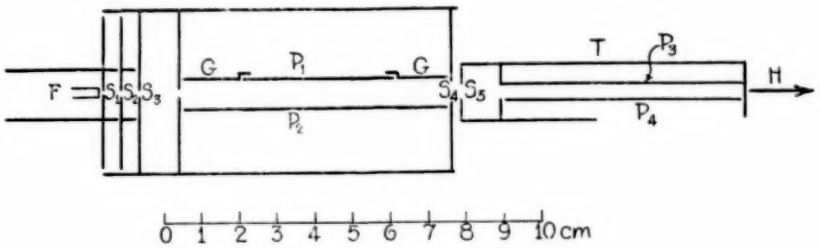


Fig. 1. Diagrammatic sketch of the apparatus.

The IR drop across this 0.034 cm length of the filament was less than 0.02 volt so that the velocity distribution of the electrons was determined almost entirely by the temperature of the filament.

The positive end of the filament was connected to S_1, which in turn was maintained about 7 volts negative with respect to S_2. The velocity of the electrons was determined by a variable potential between S_2 and S_3.

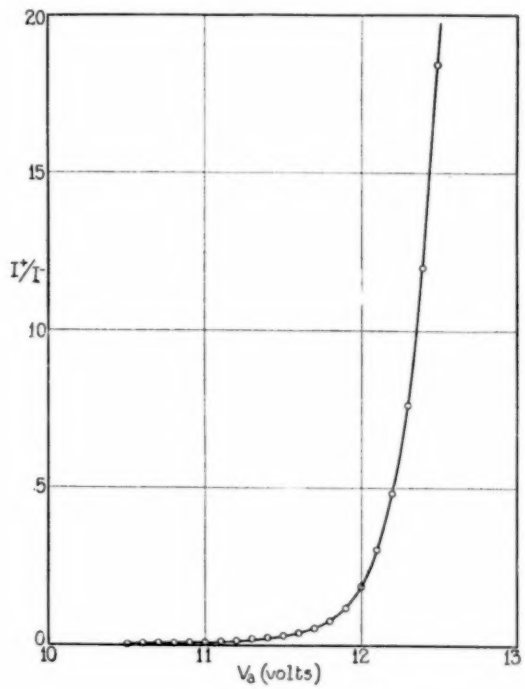
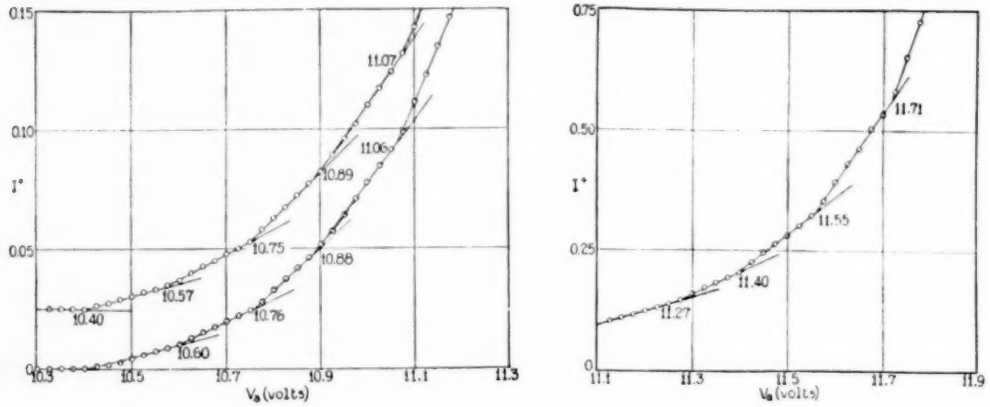
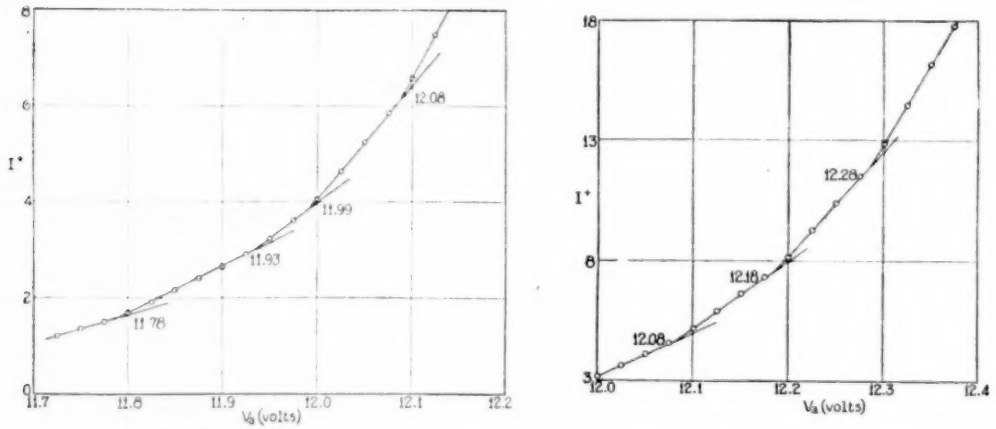


Fig. 2. The efficiency of ionization by electron impact of Hg vapor near the ionization potential. The ordinates represent the efficiency in arbitrary units.

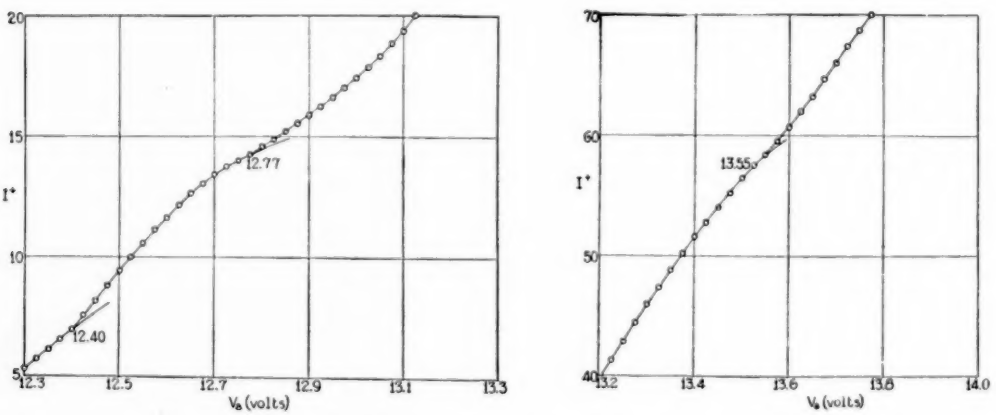
This arrangement gave an electron beam whose magnitude was quite independent of the field between S_2 and S_3 and insured a voltage correction which was independent of the speed of the electrons.



Figs. 3 and 4. The ionization of Hg vapor by electron impact from 10.4 to 11.7 volts. I^+ is proportional to the efficiency of ionization.



Figs. 5 and 6. The ionization of Hg vapor by electron impact from 11.7 to 12.3 volts. I^+ is proportional to the efficiency of ionization.



Figs. 7 and 8. The ionization of Hg vapor by electron impact from 12.3 to 13.8 volts. I^+ is proportional to the efficiency of ionization.

The holes S_2 and S_3 were about 0.18 cm in diameter, whereas S_4 and S_5 were 0.6 cm and 0.5 cm in diameter, respectively. The plates P_3 and P_4 were about 6 cm long and 3 cm wide. Plate P_4 was 0.5 cm below P_3 and was maintained 300 volts positive with respect to P_3. With the magnetic field, H, equal to 300 gauss, it is quite improbable that an electron will leave the trap, T, once it has entered, as both experiment and theory show.

Results

Fig. 2 shows the efficiency curve for the first 2 volts above the ionization potential. The ordinates are proportional to the efficiency of ionization. The curve indicates that the ionization does not rise sharply at the ionization potential, the rapid rise occurring almost a volt above this potential. Curves obtained with a poor velocity distribution did, however, show a more rapid rise at 10.40 volts.

Figs. 3–8 show the efficiency curve plotted on a large scale. (They are not all plotted to the same scale.) The accuracy with which the breaks could be reproduced is shown in Fig. 3 where two independent sets of data have been plotted.

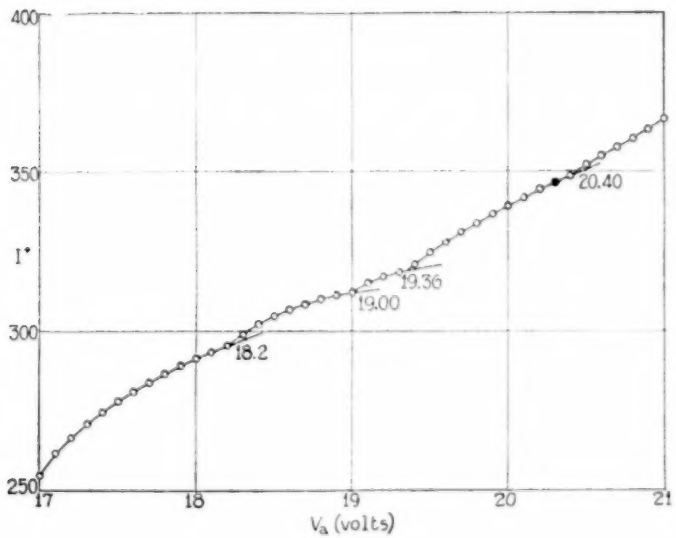


Fig. 9. The ionization of Hg vapor by electron impact from 17 to 21 volts. I^+ is proportional to the efficiency of ionization.

From 13.8 to 18 volts the curves were smooth and showed no obvious discontinuous changes in the slope. Fig. 9 shows the curve from 17 to 21 volts. The four breaks in this interval could be reproduced very accurately. Beyond 21 volts evidences of breaks were observed but the experimental errors in the measurements were greater than the deviations from a smooth curve, so that no satisfactory results were obtained although it is believed that several critical potentials do exist beyond 21 volts. However, at 29.5 volts a definite in-

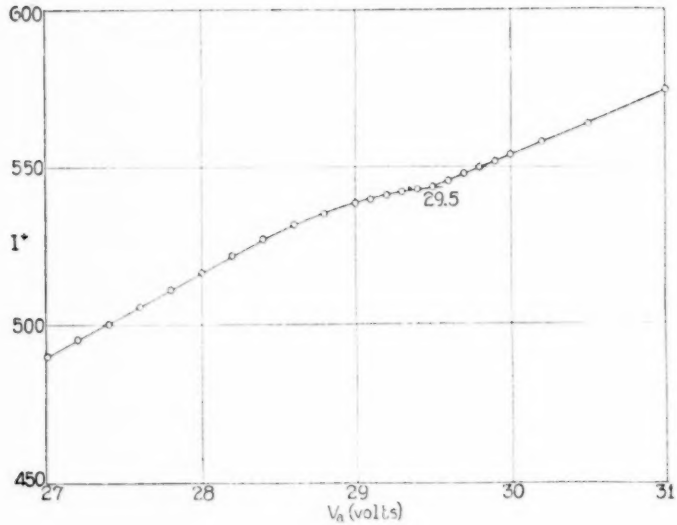


Fig. 10. The ionization of Hg vapor by electron impact from 27 to 31 volts. I^+ is proportional to the efficiency of ionization.

TABLE I. *The "ultra-ionization potentials" in Hg vapor.*

Lawrence	Hughes and Van Atta	Haupt*	Nielson and Potter	Author
10.40	10.40	10.40	10.40	10.40
10.60	10.62			10.60
			10.66	
				10.76
	10.88			10.88
			11.00	
				11.06
11.29				11.27
	11.40		11.41	11.40
				11.55
11.70			11.72	11.70
	11.77			11.78
				11.92
				12.00
12.06			12.06	12.06
	12.16			12.17
		12.30		12.28
			12.40	12.40
		12.45		
	12.76		12.80	12.77
		12.85		
		13.20	13.25	
				13.55
				18.20
				19.36
				20.40
				29.50

* Haupt reports that he also observed those found by Lawrence.

crease was always observed, which may be attributed to the formation of Hg^{++}. Fig. 10 shows a typical set of data in this region.

A list of the critical potentials reported by the various investigators, together with those found by the writer, is given in Table I. The values given in the same row were assumed to correspond to the same critical potential. The agreement is in general very good.

An "ultra-ionization potential" at 11.06 volts has not been previously reported, but as Fig. 3 shows, it apparently represents the minimum energy necessary for some quite efficient mode of ionization. It is of interest to note that in a study of the electron energy losses in mercury vapor, Castle W. Foard[9] found a pronounced peak which corresponded to a loss of 11.07 volts of energy. He was unable to account for this loss on spectroscopic grounds. This loss of energy can probably be associated with the ultra-ionization potential at 11.06 volts if we assume that ionization can result as a consequence of the simultaneous excitation of the two valence electrons. This would require a quantized energy loss.

The measurements of the positive ion current were made with a Compton electrometer having a sensitivity of about 3700 mm per volt. The electron current used in obtaining the data for the curves shown in Figs. 3–10 was about 5×10^{-8} amperes and for some of the work was measured with a galvanometer having a sensitivity of 2.70×10^{-11} amperes per mm deflection by employing a suitable balancing-out arrangement. With this sensitive measuring device, very small variations in the electron current could be detected. A very careful study showed that there was no correlation between any observed deviations in the electron current and the observed critical potentials.

TABLE II. *Efficiency of ionization, ϵ expresses as number of positive charges per electron per cm path per mm pressure at 0°C for various electron velocities.*

V_a (volts)	ϵ	V_a	ϵ	V_a	ϵ	V_a	ϵ
15	3.43	75	19.33	175	17.55	475	11.45
20	8.14	80	19.38	200	16.90	500	11.05
25	11.51	85	19.40	225	16.30	525	10.70
30	13.68	90	19.38	250	15.70	550	10.45
35	15.37	95	19.32	275	15.15	575	10.15
40	16.42	100	19.25	300	14.60	600	9.88
45	17.38	105	19.17	325	14.10	625	9.63
50	17.90	110	19.07	350	13.55	650	9.36
55	18.51	120	18.83	375	13.05	675	9.12
60	18.85	130	18.64	400	12.55	700	8.90
65	19.05	140	18.40	425	12.15	725	8.70
70	19.25	150	18.15	450	11.77	750	8.55

The pressure used ranged between 3×10^{-5} and 1.85×10^{-4} mm mercury. The data shown in Fig. 11 and in Table II were taken with a pressure of 8×10^{-5} mm of mercury and agrees very closely with data taken at different pressures. The ordinates represent the total number of positive charges per electron per cm path reduced to a pressure of 1 mm of Hg at 0°C. The posi-

[9] C. W. Foard, Phys. Rev. **35**, 1187 (1930).

tive ion current for these data was measured with a galvanometer having a sensitivity of 2.70×10^{-11} amperes per mm deflection. The electron current used was about 6×10^{-7} and was measured with a galvanometer having a sensitivity of 8.00×10^{-10} amperes per mm deflection.

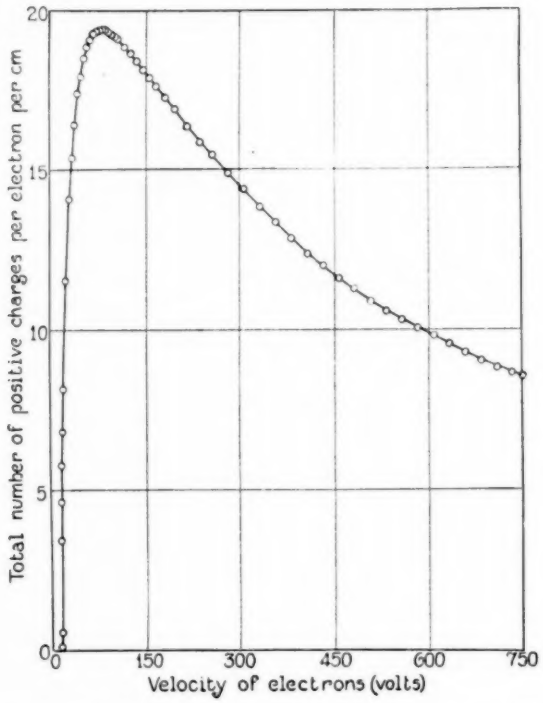


Fig. 11. The total number of positive charges per electron per cm path at 1 mm pressure and 0°C plotted as a function of the velocity of the impacting electrons in volts.

Discussion

It is very difficult to reconcile the values for the efficiency of ionization of mercury vapor given here with those obtained by Bleakney and by Jones, both of whom employed the same method. The present work was carried out with a better vacuum and a very careful study of all of the characteristics of the apparatus failed to reveal any objectionable features in the apparatus, method, or procedure. It is interesting to note that the copper apparatus, used in the study of helium, neon and argon, gave essentially the same values for Hg vapor as those given here.

The author takes this opportunity to acknowledge the constant interest and many suggestions of Professor John T. Tate.

OSCILLATIONS IN THE GLOW DISCHARGE IN ARGON

By Gerald W. Fox
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(Received February 16, 1931)

Abstract

Report is made of radio frequency oscillations observed in argon glow discharges. The frequencies lie in the range of 10^4 cycles/sec to 10^5 cycles/sec in approximate harmonic relations. They are very sensitive to pressure changes but appear to bear no relation to the tube current. The peculiar action of a magnetic field on the oscillations is described. Some frequency calculations are made on the assumption that the potential distribution throughout the Faraday dark space can be represented by a parabola.

SOME time ago the writer[1] described experiments with oscillations observed in hot cathode glow discharges in neon. The present paper deals with a continuation of the same type of work in argon. The same discharge tube was used except that direct current was employed on the heater coil, since it was found that the a.c. introduced an extraneous sixty-cycle modulation. The argon was purified by a lengthy exposure to the action of a mischmetal arc. The experimental procedure was in all respects like that previously described.

Characteristics of the Discharge

The discharge in argon was steadier than in neon. The color appeared very nearly white to the eye but the brightness of the discharge for a given power input was not nearly so pronounced as in neon, while the heating was much greater. In neon, a current of 20 amperes could be run for a short interval and 10 amperes was possible continuously, with ordinary fan and water cooling. With argon, however, a current of two amperes caused the heavy copper anode to glow red in less than a minute and for this reason no observations were possible with currents larger than four amperes.

The pressure range over which oscillations were observed was quite narrow, the limits being approximately 0.2 mm Hg to 1.0 mm Hg. It was impossible to obtain oscillations for random current values in this pressure range. Oscillations were present only for particular values of current and pressure and when observed their frequency appeared to be independent of the tube current. As in the case of neon the discharge must be steady to exhibit oscillations. The slightest flickerings on anode or cathode produce enormous irregularities which are detected as "static" noises in the pick-up circuit. If one starts in at low pressure values a discharge may be maintained in argon at as low as 0.001 mm Hg but as listened to it is very noisy and the glow is feeble. With increasing pressure no noticeable change occurs in tube current,

[1] Fox, Phys. Rev. **35**, 1066 (1930).

tube voltage, or glow until a pressure of about 0.1 mm Hg is reached, when the light from the tube suddenly increases many times and the discharge becomes noiseless except for a slight hiss. Tuning through the frequency range then shows the presence of oscillations which seem to start simultaneously with the increase of light from the tube.

The maintaining voltage for the argon discharge averaged about 255 volts which is approximately 75 volts higher than the maintaining voltage for neon.

As in the case of neon the interesting flashes described by Whiddington[2] and Aston and Kikuchi[3] were generally present.

Results

1. Frequencies present at a given pressure.

Tables I and II show typical data on frequencies present in the discharge. As in the case of neon these frequencies seem to be harmonics of one particu-

Table I. *Frequencies present in glow discharge in argon.*

(Tube current 2.6 amperes, tube voltage 255 volts, gas pressure 0.77 mm Hg).

Wave-length (meters obs.)	Frequency (cycles/sec calc.)	Order
23,200	12,930	2
15,600	19,230	3
11,400	26,320	4
5,830	51,500	8
5,200	57,700	9
4,620	65,000	10
4,215	71,200	11
2,890	103,700	16
2,390	125,600	19
1,640	182,900	28

lar frequency though this could not be observed due to the limited tuning range. In no instance was a complete series of harmonics observed nor was there exhibited any preference for particular omissions.

Table II. *Frequencies present in glow discharge in argon.*

(Tube current 1 ampere, tube voltage 254 volts, gas pressure 0.68 mm Hg).

Wave-length (meters obs.)	Frequency (cycles/sec calc.)	Order
20,980	14,340	2
14,000	21,430	3
10,460	28,670	4
5,930	50,700	7
4,650	64,500	9
3,725	80,700	11
3,215	93,400	13
2,775	108,300	15
2,625	114,300	16
2,460	122,000	17
2,220	135,100	19
1,980	151,500	21
1,915	156,500	22

[2] Whiddington, Engineering **120,** 20 (1925).

[3] Aston and Kikuchi, Proc. Roy. Soc. **A98,** 50 (1920).

2. Variation of oscillation frequency with pressure.

In the argon discharge, the frequency range covered was not as wide for a given pressure difference as in neon. A noticeable peculiarity was that the discharge frequency changed almost linearly with the pressure down to a certain critical value when no further change could be produced, the frequency remaining constant but becoming weaker until, on further pressure reduction, it broke completely. (Fig. 1.)

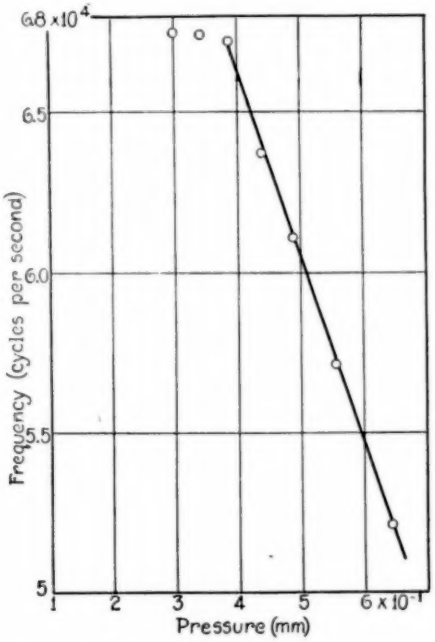

Fig. 1. Variation of oscillation frequency with pressure.

3. Relation of frequency to tube current.

It was not possible to show any frequency dependence on tube current such as appeared in neon. Having set on a particular frequency, this frequency persisted within a few cycles of the same value while the current was changed as much as an ampere when the oscillation would stop suddenly, to start again when the current was returned to its former original value.

4. Effect of a magnetic field on oscillations.

Some peculiar effects were noticed when a magnetic field was placed at right angles to the discharge. When a horseshoe magnet was moved from the anode end of the discharge toward the cathode, the frequency of the beat note in the telephone receiver fluctuated periodically from zero to a maximum, while moving the length of the positive column as shown in Fig. 2. On coming to the Faraday dark space, the regular oscillations disappeared altogether and the discharge became very noisy. Upon the removal of the magnet, however,

the discharge became quiet again and the oscillations reappeared after a time of the order of thirty seconds. This observation was made repeatedly.

Discussion

From the work of Compton, Turner, and McCurdy[4] we have a fairly good picture of the potential distribution throughout the glow discharge. They have shown the existence of a potential minimum in the Faraday dark space, especially in cases of large ionization. In the discharges in both argon and neon, the tube currents were of the order of several amperes so that we may expect a large concentration of positive ions in the negative glow, for the ionization processes going on are more effective than the needs of the circuit as a whole demand. Positive ions from the cathode end of the positive column and from the negative glow, will both be accelerated into this region of minimum potential. This accelerating field is really necessary to prevent the ac-

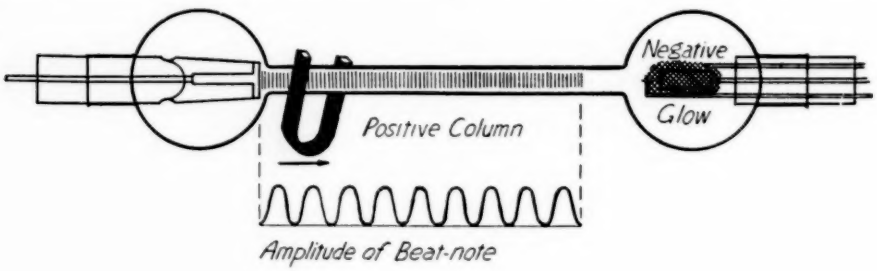

Fig. 2. As the magnet is moved along the positive column the sound in the telephone receiver fluctuates regularly in intensity.

cumulation of a negative space charge here by diffusion of electrons from the negative glow. The positive ions from the positive column and probably also those from the negative glow approach the potential minimum with terminal velocities attained in the fields through which they have travelled and, since these fields are rather weak, their velocities will be small. Thus some ions will be trapped for a time and we may imagine them oscillating about the potential minimum until they acquire sufficient energy to get over the hump on the cathode side. An ion's escape probably comes suddenly after a collision with a molecule or another ion which provides a suitable energy transfer.

The action of the magnetic field in the Faraday dark space lends some support to this idea of the origin of the oscillations. When the field is applied here, the additional magnetic force to which the ions are subjected, upsets the regularity in their motion and brings about the noise that is heard in the pick-up circuit. The high-frequency oscillatory component of the tube current is really very small. It is merely superimposed upon the main steady current through the tube. The fact that the frequency increases with decreasing pressure seems reasonable for we can imagine fewer collisions taking place to slow the ion down while it remains in motion about the potential minimum.

[4] Compton, Turner, and McCurdy, Phys. Rev. **24,** 597 (1924).

The action of the magnetic field throughout the positive column makes one think of the presence of standing waves. It seems possible that electric sound waves of the type mentioned by Tonks and Langmuir[5] may be present, since the observed frequencies fall within the range of their calculations. The flashes, observed by Whiddington,[2] which travel from anode toward cathode, and which are of low frequency and can be observed with a rotating mirror, can be explained by assuming the presence periodically of a large anode drop which produces excess ionization in the anode sheath. This excess of positive ions would travel toward the cathode, modifying the potential distribution as they go and causing local ionization and excitation. This would appear as a travelling striation.

Simple Theory of Oscillation in the Glow Discharge

If one assumes as a first approximation that the curve representing the potential distribution throughout the Faraday dark space is a parabola, it is not difficult to arrive at an expression for the frequency of the oscillation which gives a value which is of the observed order of magnitude.

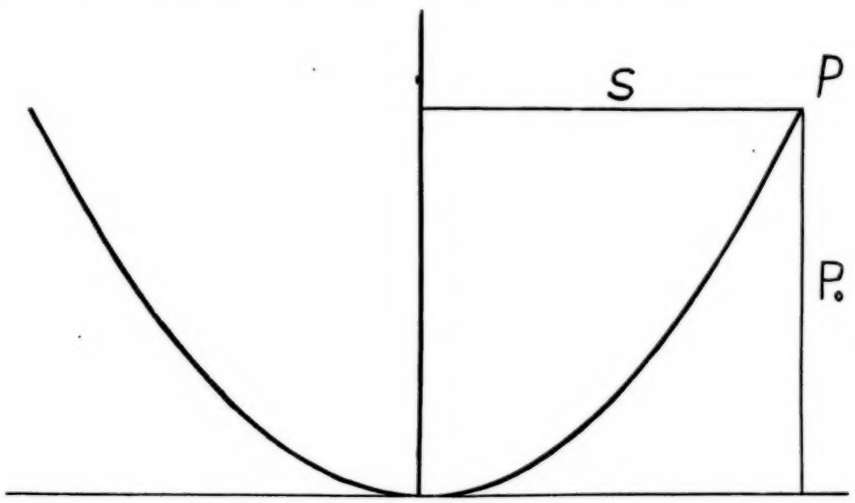

Fig. 3.

Let P represent the potential according to the equation $P=4ax^2$. Then since

$$\frac{m}{2}\left(\frac{dx}{dt}\right)^2+4aex^2=W,\quad \frac{d^2x}{dt^2}+\frac{8ae}{m}x=0.$$

The solution to this equation gives

$$x=C\cos(8ae/m)^{1/2}t+D\sin(8ae/m)^{1/2}t$$

in which it is seen that x repeats itself at intervals of 2π in the time $(8ae/\mathrm{m})^{1/2}t$ The period of a complete vibration is $2\pi(m/8ae)^{1/2}$ and the frequency is the

[5] Tonks and Langmuir, Phys. Rev. **33,** 195 (1929).

reciprocal. The quantity a can be determined from estimates of dimensions of the Faraday dark space in the discharge. Thus assuming the dark space to be 4 cm wide and 20 volts deep, which is not unreasonable, we can write $P_0 = 4ax^2$, $a = P_0/4x^2$, or $a = 10^{-3}$ esu/cm^2 approximately. Taking e/m for hydrogen as 3×10^{14} esu/gram and 40 as the atomic weight of argon, the calculated frequency is 4×10^4 cycles per second. This is of the observed order of magnitude. The frequency appears to be quite dependent on the ratio of the width of the pit to its depth in volts. On the other hand, the frequency, is not very dependent on the type of ion in the discharge. The e/m for argon is of the same order of magnitude as e/m for neon. As mentioned before, the observed oscillations for both gases occurred in the same range.

The presence of a series of harmonic frequencies indicates that the potential distribution is not so simple a function as has been assumed. We do not know the actual potential distribution throughout the Faraday dark space, but since a slight distortion of our assumed distribution would allow the presence of harmonics, their presence can thus be accounted for.

In conclusion, the writer wishes to thank Professor H. M. Randall, director of the Physics Laboratory of the University of Michigan, for extending the privileges of the laboratory, where the experimental work was done.

THE RELATIVE INTENSITIES OF MERCURY LINES UNDER DIFFERENT CONDITIONS OF EXCITATION

By Marcel J. E. Golay
University of Chicago

(Received December 15, 1930)

Abstract

The relative intensities of the lines of the $2s-2p_i$ triplet have been measured by a photographic method with a calibrated tungsten lamp as a standard of comparison. The intensity ratios have been found to vary with conditions of excitation due to the absorption of the 5461 and 4047 lines by atoms in the metastable states $2p_1$ and $2p_2$. About three-quarters of the 5461 radiation and about one-third of the 4047 radiation were absorbed in a commercial mercury-filled tube with three electrodes when a high plate current was passed through the tube. A lesser absorption was found when an ordinary arc was used and when small plate currents were passed in the three-electrode tube. A tube specially built to excite mercury by electronic bombardment and provided with means for controlling the mercury pressure gave uniform results under various conditions of mercury pressure and plate current, and the double ratio of 8.5:3.3:1 was found for the intensities divided by the fourth powers of the corresponding frequencies. The ratio of 4078:4047 was found to vary with plate voltage in a manner similar to the variation of efficiency of ionization with electron velocity. It was attributed to the presence of two mechanisms of emission giving widely different intensity ratios, namely, excitation of the neutral atom to a higher energy level, and recombination of the ionized atom. A roughly quantitative survey of the intensities of the excitation and of the recombination spectra indicated that in comparison with atoms excited to a higher level by electronic impact as occurs in the arc, recombined atoms will prefer the singlet to the triplet system, while within each system their order of preference is P, S, D, and p, s, d, respectively. Also, within each state, a level at about the height of the $4S$ level is preferred to the others.

General

THE purpose of the research reported here was primarily the study of the $2s-2p_i$[1] triplet. The intercombination line $2S-2p_2$ of wave-length 4078 was also included in this study because of the work of Houston,[2] who treats the lines $2S-2P$, $2S-2p_2$, $2s-2P$ and $2s-2p_i$ (i=1, 2, 3) as a whole. According to this author the ratio 5:3:1 must be found for

$$\frac{A(5461)}{N_3}:\frac{A(4358)}{N_3}+\frac{A(4078)}{N_1}:\frac{A(4047)}{N_3},$$

where A designates the intensity divided by the fourth power of the frequency and N the number of atoms in the respective initial states. The quantities written above are proportional to the squared amplitudes of the corresponding lines, and it is for these squared amplitudes that the "sum-rule" must hold.

[1] Notation of Paschen.
[2] W. V. Houston, Phys. Rev. **33**, p. 297 (1929).

The squared amplitudes of the individual lines can also be determined from the formulas given by Houston. They give approximately the ratio 5:2.9:1 for the relative intensities of the triplet lines, divided by the fourth powers of the corresponding frequencies. They also give the ratio of 0.1:1 for the lines 4078 and 4047. This signifies that for an equal population of their respective initial levels, line 4078 will have approximately one-tenth the intensity of line 4047, the relative intensities of these two lines giving thus a basis for a computation of the relative population of their respective initial levels.

Method of Intensity Measurements

When two lines are but a few angstroms apart in wave-length, their relative intensities may in principle be measured by weakening one line by a known amount until it has the same intensity as the other, that is, until the blackening of the photographic plate is the same for the two lines. Usually both lines are weakened by a series of absorbing screens, and their relative intensities are obtained through some process of interpolation which affords at the same time a number of results, which must verify each other, when the image of the weaker line through the clearer weakeners is comparable in intensity to the image of the stronger one through the more opaque portions.

When the lines to be compared are sufficiently separated to warrant a determination of the sensitivity of the emulsion for the corresponding wave-lengths, a source of known spectral distribution such as a black body or an incandescent filament of known temperature and emissivity is used for this purpose. Each line is then compared with the continuous radiation of the same wave-length. This can of course be done as before, by means of weakeners, calibrated for each of the different wave-lengths of the group under study.

Their use, however, can be avoided very simply by using the standard of comparison to put on the plate a series of intensity marks of known relative intensities. As the standard of comparison emits a continuous spectrum, the gradation of intensities can be obtained by varying the width of the slit, and if a lens is used to focus on the slit an image of the tungsten ribbon of the lamp used as a standard, one can also place diaphragms of known geometrical transmission in front of the lens.

A lower limit for the slit-width is set by the accuracy with which this width can be measured, and by the size of the diffraction pattern formed on the prism. It is desirable that the main fringe and at least one or two lateral fringes appear on the prism when sighting it from the camera side of the spectrograph, in order to avoid losing more than a few percent of the light. Conversely, the largest slit-width must not allow the integrated spectrum thus obtained to misrepresent the intensity of the source, and the sensitivity of the emulsion. According to Ornstein no errors due to the integration of the spectrum will be appreciable if the width of the slit corresponds to less than 60A on the plate for any of the wave-lengths studied.

The diaphragms placed in front of the lens must cover enough of the latter so that a full image of the uncovered portion can be seen on the prism from

the camera side, while if but little light is desired, these diaphragms must have holes not small enough to create on the slit a main fringe equal in width to the difference between the image of the filament and the opening of the slit.

When a set of intensity marks has been put on a plate it is necessary to take only one spectrogram of the source of light, taking care to use a rather wide slit, and to compare the lines with the comparison spectrum at the same wave-length. One can thus take many exposures on one plate, which is advantageous when studying the variations of relative intensity with certain conditions of experimentation. One obtains indeed but one figure for every exposure, while several are obtained when the source is photographed through a series of weakeners. If it is desired to obtain a few figures for every condition of light emission studied, one has to take as many exposures, preferably using various diaphragms in front of the lens projecting an image of the source on the slit.

In the work reported here, care was taken that light from all sources photographed followed the same optical path. As an added precaution it was

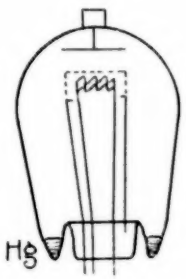

Fig. 1. Diagram of mercury-filled tube.

also verified that the transmission of the whole optical system was sensibly the same along the optical axis and away from this axis.

As sources of known radiation incandescent lamps with a flat tungsten ribbon were used and their temperatures determined photographically by comparison with a standard of known temperature and emissivity, supplied to Ryerson Laboratory by Dr. Forsythe of Nela Park. The secondary standards were generally operated at 2780 to 2800°K, and the time of exposure was the same for the standard and for the spectrum studied, to avoid errors due to a difference in Schwarzchild's constant for different wave-lengths. The radiation emitted by the standard lamp was calculated from the black body radiation formula. Corrections for the emissivity of tungsten at 2800°K at various wave-lengths were introduced. Corrections were also introduced for the dispersion of the spectrograph and for a difference in broadness of the lines due to different distances of the plate from the camera lens.

Sources of Light and Results, $2s - 2p_i$ Triplet

Some preliminary measurements were carried out, with a home-made arc, a Cooper-Hewitt arc, and a mercury-filled tube, obligingly furnished by the Bell Telephone Laboratories. Fig. 1 shows a schematic drawing of this tube.

The spectrum of the ordinary arc was photographed at various time intervals, beginning at the moment the arc was started, and continuing until the steady state was attained. It was then observed that the ratio of 5461:4047 increased from about 4 to about 7, while the ratio of 4358:4047 decreased from about 5 to about 3. Similar results were obtained for the Cooper-Hewitt arc. Table I shows a set of results obtained similarly for the tube furnished by the Bell Telephone Laboratories, by observing the white streaks emerging from the grid at a potential just sufficient to maintain an arc.

TABLE I *I/ν^4 values for lines from tube shown in Fig 1.*

Condition of tube	5461:4047[3]	4358:4047
First exposure, tube cold	5.1	3.7
	5.6	3.7
	5.8	3.8
	6.8	3.6
	7.4	3.5
	7.3	3.4
Last exposure, tube hot	7.4	3.4

The results to be discussed later suggest the following explanation of these figures. It will be shown that the true intensity ratio is about 8.5:3.3:1. The lines 5461 and 4047 are, however, absorbed by the atoms in the metastable states $2p_1$ and $2p_3$. As the line 4358 terminates on the level $2p_2$ where the strong resonance line 2537 originates, it seems plausible to assume that the population of the $2p_2$ level is not large enough to cause any appreciable absorption of the line 4358. The population of the metastable states is roughly proportional to the ratio of the rate at which these states are reached by the excited atoms, to the rate at which they leave them owing to collisions of the second kind. The rate at which atoms are sent into metastable states is roughly proportional to the current, while the rate at which they leave them increases with the number of collisions per unit time; this number increases about linearly with the temperature, and the density, this latter quantity rising rapidly with the temperature. It can therefore be expected that at a low pressure, the ratio of 5461:4047 will be considerably reduced, line 5461 being much more absorbed than line 4047 on account of the greater population of the state $2p_1$, while the ratio of 4358:4047 will be found somewhat too high on account of the absorption of line 4047. As the temperature and the pressure increase these ratios will approach their true values, due to the diminished population of the metastable states, as can be verified in the above table.

The following tables show a typical set of results susceptible of similar interpretation. The temperature of the tube was kept approximately constant during the observation. The time of exposure for the spectrum and for the standard light was the same for each plate. Diaphragms were placed in front of the condensing lens to reduce the very different intensities photographed to approximately the same level of blackness on the plate.

[3] All ratios given in this article refer to the intensities divided by the fourth powers of the frequencies.

TABLE II. *I/ν^4 ratios for constant tube temperature but varying plate current.*
(Observation of light emitted between grid and plate)

Plate current	5461:4047	4358:4047
1.0 amp.	3.2	
1.0	3.6	4.9
0.27	5.9	4.4
0.27	5.0	4.3
0.0075	8.1	4.0
0.0065	7.9	3.9
0.0055	8.3	3.9
0.004	9.0	3.7

The explanation of these results is obvious. A higher plate current increases the rate at which atoms are thrown into metastable states, and higher absorption of line 4047, and especially of line 5461, results therefrom.

From the foregoing it appears that the Hg density affects the results in a two-fold manner. A direct effect of higher density would be a more rapid elimination of the metastable states, thus reducing the effect of absorption in the intensity ratios. This first effect would be masked, however, by the more complicated and more intense phenomena accompanying high pressures.

Determination of the true intensity ratios of the triplet. The facts mentioned above were not apparent at the time these experiments were carried out, for it was expected that the ratio 5:3:1 would be found for the relative intensities of the triplet divided by the fourth powers of the frequencies, and ratios higher than 5 for lines 5461 and 4047 could not be explained by an absorption of line 5461. At the same time it was obvious that the absorption of line 4047 was much less than the absorption of line 5461, for the population of the $2p_1$ state is much larger than the population of the $2p_3$ state, and this theoretical prediction was confirmed by the comparatively smaller variations of the ratio of 4358:4047. Also, the glass of the three-electrode tube used was not very clear, and had a larger transmission for the 5461 line than for the other lines of the triplet.

A tube was then built, with means for controlling the Hg pressure, and with a quartz window for the eventual study of the ultraviolet lines.

This tube is shown in Fig. 2. Electronic emission was provided by a tungsten filament. The leads into the tube were tungsten rods, while the other metallic portions were of nickel. A plate, P, with a rectangular hole cut to correspond to the opening, A, of the cage was inserted as shown in the figure, to prevent the white light of the filament from reaching the slit of the spectrograph. A number of spectra were taken with the end, B, of the cage open, so that a considerable amount of light due to the blue glow filling the tube contributed to the radiations photographed. Any amount of shielding in the far end of the tube failed to eliminate this glow. As it was thought that this glow was due to a somewhat different mode of excitation from that which produced the light in the cage by electrons of a definite velocity, the far end of the cage was subsequently closed, as shown in the figure. This was done by means of a little strip of platinum, blackened in the flame of a match. A

small strip of nickel, C, was welded over the far end of the grid to prevent a direct illumination of this end wall by the filament. At the time this change was effected, the nickel grid of rather coarse mesh, hitherto used, was replaced by a nickel grid of the finest mesh obtainable. This was done for the purpose of obtaining a more uniform flow of electrons in the cage, and surprisingly enough this new grid stood higher currents than the coarse one formerly used, without showing any trace of deterioration. In spite of the electrical screening provided by the shield, S, and the front plate, P, the space, F, in the front end of the tube was filled with a weak glow, the part of this glow in the prolongation of the cage contributing, therefore, to the light photographed.

The Hg pressure in the tube was indirectly controlled by placing the Hg trap in a beaker of water of a certain temperature.

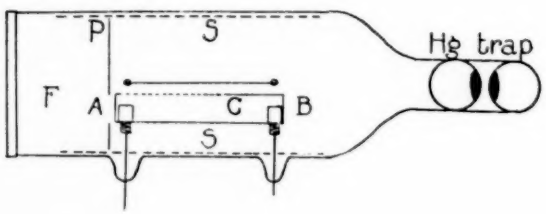

Fig. 2. Diagram of apparatus.

A thorough baking out of the tube was found necessary to avoid nitrogen and carbon monoxide bands. This was done by wrapping asbestos around the tube and letting a plate current of 0.8 to 1 amp. flow under a potential of about 200 volts for a few hours. Even though the CO bands were observable at the end of this period, they would quickly disappear after the asbestos had been removed and the tube brought to its normal running temperature.

A few refinements were introduced in the method of intensity measurements. They are outlined below.

A little strip of gray glass was placed in the camera on the path of line 4358, in order to bring this line to the same blackness level as lines 4047 and 5461. As this line and the standard radiation for its measurement were both modified in the same manner, no change was called for in the method of measurement. While more accurate, the results thus obtained for the 4358:4047 ratios agreed well with a number of results obtained before this precaution was taken. About 40 exposures were taken on each plate, a little less than half this number being assigned to the intensity marks. Two was chosen for the ratio of the geometric progression of intensities, and two or three exposures were taken for each intensity, the slit width and the number of holes used in the diaphragm being both varied so as to check the method used, and to reduce chance errors due to setting and variations in the emulsion. (The different measurements of blackness for marks of the same theoretical intensity proved to be closely grouped in the great majority of cases.) Also, each condition of plate current and plate voltage studied was photographed two

or three times, as the light intensity permitted, using the diaphragm with maximum openings, and others of one-half and one-quarter the area of the first. As a last precaution, all plates were wiped continuously while in the developer, to insure uniformity of development.

Two current values, 0.3 and 0.6 amp. were used under various voltages to bring out any systematic dependence of the intensity ratios observed upon the plate current, as well as to bring out any voltage dependence for any one fixed current, especially with reference to the 4078:4047 ratio.

The narrow range of Hg temperature explored (limited for the high temperature by the coolest point of the tube to avoid condensation in this point, and for the low temperature by the light intensity fit for convenient exposures) was considered wide enough to detect any dependency upon pressure on account of the comparatively large range of pressures corresponding to these temperatures.

No dependence upon plate current, plate voltage and Hg pressure was found for the relative intensities of the triplet, while the ratio of 4078:4047 showed a marked dependency upon plate voltage.

The averages obtained for the triplet are given in Table III.

TABLE III. *I/v^4 values for triplet lines obtained with tube shown in Fig. 2.*

Plate No.	Temp. of Hg	4358:4047	5461:4047
14	100°C	3.3	8.3
22	0	3.0	8.5
23	22	3.3	8.5
"	60	3.4	
25	20	3.2	7.8
29	20	3.2	8.8
"	40	3.3	7.9
30	40	3.4	7.9
31	22		9.2
34	23		8.8
35	41.5	3.3	8.6
36	25		9.5
37	24		8.5
		Average 3.3	8.5

The experimental error attached to the average given for the ratio of 5461:4047 is probably larger than for the other one, but should not exceed 10 percent, assuming, however, that the temperature of the lamp used as standard is correct.

RATIO OF 4078:4047 AND GENERAL STUDY OF THE ELECTRONIC BOMBARDMENT EMISSION

As mentioned above, the ratio of 4078:4047 varies with plate voltage. This is shown in Fig. 3, where this ratio has been plotted as a function of the plate voltage from the data obtained from five plates. These curves point to a rapid rise to a maximum, reached at about 100 volts, and then a slow downward trend.

The existence of a variation in relative intensity of two lines makes it necessary to assume the operation of at least two different mechanisms—if there were only one, the absolute intensity might vary, but not the relative. Each of these mechanisms will presumably be operative in producing both lines, but with a different ratio of intensities. The ratio measured will be some weighted average of the ratios which are characteristic of each of these mechanisms.

This variation with voltage is strikingly similar to the variation of the efficiency of ionization as found by a number of authors. For the purpose of comparison, the probability of ionization of mercury atoms by electrons has been plotted as the dotted curve. It was obtained from Bleakney's[4] data by adding the ordinates of his curves for the probability of single, double, and triple ionization. It also represents the variation in the intensity of the light due to atoms which have been ionized and recombined with electrons if it be

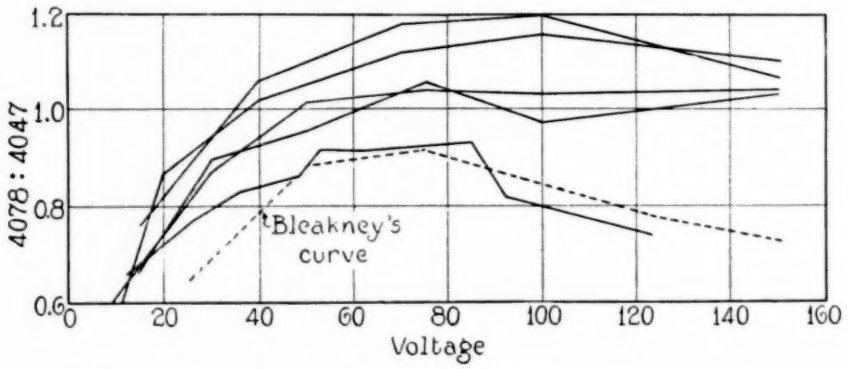

Fig. 3. Ratio 4078:4047 plotted as a function of the plate voltage from data obtained from five plates.

assumed that doubly and triply ionized atoms recapture successively, two and three free electrons respectively from the negative space charge inside the cage.

The parallelism of this curve with the ratio of 4078:4047 seems to suggest the following explanation. Atoms which have been previously ionized will emit a recombination spectrum with a comparatively larger ratio of 4078: 4047 than excited atoms, while the observed ratio will vary somewhat parallel to the amount of light emitted which is due to recombined atoms, if the number of excited atoms is assumed to have no variations, as marked as the one shown by Fig. 3, beyond the ionization potential. This explanation would be supported by the fact that many ionized Hg lines were quite conspicuous at the higher voltages used (40 volts and above), while the presence in the cage of slow secondary electrons made conditions favorable for the recombination of Hg ions.

If the large differences found between the intensity distributions in an

[4] Bleakney, Phys. Rev. **33,** 139 (1930).

ordinary arc and in an electronic bombardment spectrum were attributed to the presence in the latter of a recombination spectrum certain consequence would follow which are brought out by Table IV. This table has been prepared from a table giving the intensities of the lines in an electronic bombardment spectrum at 70 volts using the intensities of the lines of an arc spectrum as units. All the values obtained for lines originating at a certain level have been averaged, and these averages have been given in Table IV. This table therefore gives an estimate of the population of the various levels in an electronic bombardment spectrum in comparison with an arc spectrum. According to what has been said above Table IV would indicate that by comparison

TABLE IV. *Relative population of levels—electronic bombardment—spectrum vs. arc spectrum.*

Level	Relative Population	Level	Relative Population
$2S$	1.5	$2s$	0.15
$3S$	3.	$3s$	0.15
$4S$	11.	$4s$	0.8
$5S$	4.	$5s$	0.4
		$6s$	0.15
$4P$	55.		
$5P$	25.	$4p_1$	0.6
$6P$	2.	$5p_1$	1.4
$7P$	1.5	$6p_1$	0.6
$3D$	0.4	$3d_1$	0.14
$4D$	2.2	$4d_1$	0.15
$5D$	1.7		
$6D$	0.4	$3d_2$	0.16
$7D$	0.2	$4d_2$	0.3
$8D$		$5d_2$	0.8
		$3d_3$	0.2
		$4d_3$	0.1

with excited atoms, recombined atoms will occupy a much larger proportion of singlet terms, while within each system of terms the P-state (or the p-state), and within each state a level at about the height of the $4S$ level would be most favored in this new population distribution.

This explanation for the variation of the ratio of 4078:4047, and the consequences of this explanation, are given with much reserve, however, as it has been the conclusion reached by F. L. Mohler[5] and other authors that in a recombination spectrum the triplet terms are comparatively more populated than in an excitation spectrum.

The writer wishes to express his appreciation to Professors Monk and Eckart for the suggestion of the problem and assistance throughout the duration of the work.

[5] F. L. Mohler, Phys. Rev. Suppl. **1**, 221 (1929).

THE SPECIFIC HEAT OF METHANE

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(Received February 16, 1931)

Abstract

Two different forms have been suggested for the methane molecule by various authors. They are the symmetrical tetrahedron and the symmetrical pyramid. Calculations have been made for the values of the specific heat at constant volume for the two types of structure. It is found that neither type gives values in agreement with experiment. The curve obtained on the basis of a tetrahedral structure however gives much better agreement than the resulting curve for the pyramidal structure.

THE infrared absorption spectra of methane was investigated quite carefully by J. P. Cooley[1] several years ago. Dennison,[2] on the basis of Cooley's results and with certain other fundamental assumptions, was able to ascribe a symmetrical tetrahedral structure to the molecule.

J. Kunz[3] called attention to the fact that there was quite a difference between the specific heat of methane as calculated from this model and the experimental values.

V. Guillemin[4] has shown, however, that on the basis of certain definite assumptions as to the forces between the ions in the molecule, the potential energy for the symmetrical pyramidal configuration is smaller than the value obtained for the tetrahedral structure. Hence the pyramidal structure is more stable than the tetrahedral.

Numerous facts have been advanced by Glockler,[5] Henri,[6] and others supporting one or the other of the two alternative forms.

Each model yields fifteen degrees of freedom, three of translation, three of rotation, and nine of vibration. Moreover, each model gives four fundamental vibrational frequencies. Hence, giving to the translations and rotations their equipartition values, we obtain for the specific heat at constant volume

$$c_v = R\left(3 + \sum_{i=1}^{4} n_i \left(\frac{h\nu_i}{kT}\right)^2 \frac{e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2}\right)$$

where the n_i gives the number of degrees of freedom of the corresponding vibration frequency ν_i.

The values of ν_i and n_i are given below in Table I.

Table I. *Values of ν_i and n_i.*

ν_i	n_i	ν_i cm^{-1} Tetrahedral	ν_i cm^{-1} Pyramidal
ν_1	1	4217	7760
ν_2	2	1520	3150
ν_3	3	3014	6730
ν_4	3	1304	1990

[1] J. P. Cooley, Astrophys. Journal **62,** 73 (1925).
[2] D. M. Dennison, Astrophys. Journal **62,** 84 (1925).
[3] J. Kunz, Phys. Rev. **29,** 220 (1927).
[4] V. Guillemin, Ann. d Physik **386,** 81, 173 (1926).
[5] G. Glockler, Jour. Amer. Chem. Soc. **48,** 2021 (1926).
[6] V. Henri, Chem. Reviews **4,** 189 (1927).

Values of c_v have been calculated for temperatures ranging from 273°K to 873°K. The results together with the experimental[7] values are given below in Table II.

TABLE II. *Specific heats, experimental and calculated.*

Temp.	c_v Experimental	c_v Tetrahedral	c_v Pyramidal
273°K	6.656	6.311	5.982
373	8.738	7.188	
473	10.577	8.342	
573	12.419	9.620	7.081
673	14.288	10.855	
773	16.015	12.039	
873	17.883	13.151	9.011

The curves, Fig. 1, show the variation of c_v with temperature. The one marked *A* corresponds to the experimental values while *B* and *C* give the relation for the tetrahedral and pyramidal structures respectively. *A* and *B* are essentially linear while *C* is decidedly convex to the axis. The calculated values of c_v for the tetrahedral model agree much better with the experimental values than the values calculated from the pyramidal model.

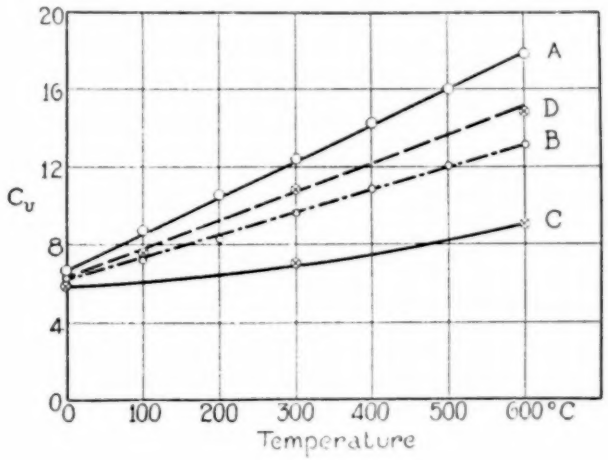

Fig. 1. Variation of c_v with temperature.

If the degrees of freedom of the vibrators with frequencies ν_3 and ν_1 are interchanged, then one obtains the curve *D* in place of *B*. These values of c_v are the maximum possible values using the frequencies given in Table I.

Undoubtedly some of the discrepancy (especially at the higher temperatures) is due to the centrifugal stretching of the molecule. This effect is not sufficient, however, to account for all the difference between the experimental and the calculated values.

It is a pleasure to thank Professor Kunz for his suggestions in regard to this work.

[7] H. B. Dixon, Proc. Roy. Soc. of London **100A**, 24, 1921–22.

THE EQUATION OF STATE OF HELIUM*

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(Received February 24, 1931)

Abstract

A brief review of the statistical theory of the equation of state is presented. Upon the basis of a recent quantum mechanical calculation of the interatomic energy, the second virial coefficient of helium has been calculated. With the use of the theoretically determined virial coefficient some properties of helium have been computed. A detailed comparison with experimental data is given.

Introduction

THE past several years have seen a great advance in our understanding of intermolecular forces. The work of Heitler and London on the resonance interaction of two hydrogen atoms suggested the nature of the repulsive force operating at small intermolecular distances to determine the effective molecular cross-section. More recently the work of Eisenschitz and London followed by that of other investigators has permitted a calculation of the polarization force, operating at larger intermolecular distances to produce the van der Waals' attraction. However the theory has so far been subjected to no critical comparison with experiment. It is the object of the present paper to make such a comparison in the case of helium, the only gas for which a fairly accurate calculation of the intermolecular energy has been carried out.

Theory of the Equation of State

Many empirical equations of state have been suggested for gases. All of them, however, may be expanded in the familiar virial form

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \tag{1}$$

where p is the pressure, V the volume of a gram-mol of gas, R the ideal gas constant, and T the absolute temperature. The coefficients, B, C, $\cdots$ are in general functions of the temperature.

Although a complete statistical theory of the equation of state has not been worked out in detail, it is possible under certain conditions to obtain a correlation between the second virial coefficient, B, and the intermolecular forces.

Above the critical temperature, it seems legitimate to assume that the fraction of the molecules in quantized collision states will be insignificant. Moreover, the Boltzmann distribution function may probably be regarded as

* Contribution No. 262.

valid for all gases until temperatures in the neighborhood of absolute zero are reached. Thus even in the case of hydrogen at a pressure of one atmosphere and a temperature of 2°K, both the Fermi-Dirac and the Bose-Einstein distribution functions give the same result as that of Boltzmann within a few percent insofar as the translational energy is concerned.[1] Subject to these limitations, it is possible to identify the sum of state with Gibbs' phase integral[2]

$$z = \int \cdots \int e^{-\overline{E}/kT} dq_1, \cdots dp_{3N} \tag{2}$$

where $\overline{E}$ is the total energy of a gas consisting of N molecules averaged over all internal coordinates and k is Boltzmann's constant. The integration is to be taken over all of the $6N$ dimensional momentum-configuration space available to the system. If the thermodynamic potential, ψ, (Helmholtz free energy function) is defined by the relation

$$\psi = E - TS$$

where S is the entropy, Gibbs has shown that

$$\psi = - kT \ln z \tag{3}$$

Moreover,

$$\left(\frac{\partial \psi}{\partial V}\right)_T = - p. \tag{4}$$

The integral (2) may be evaluated in simple form under certain conditions.[3] It is to be assumed that the density of the gas is low enough so that molecular configurations in which the fields of more than two molecules overlap, are sufficiently rare that they may be ignored. In the case of neutral gas molecules where the molecular forces are effective only at very short range, this condition is often fulfilled even at relatively high densities. Under these circumstances it is possible to write

$$z = f(T) \prod_{n=1}^{N} (V - 2nB) \tag{5}$$

where

$$B = \tfrac{1}{2} \int \int \int (1 - e^{-\bar{\epsilon}/kT}) dx dy dz.$$

Here $\bar{\epsilon}$ is the mutual potential energy of two molecules and the integration is to be taken over all values of their relative coordinates. From Eqs. (3), (4), and (5), after expansion of the logarithm in powers of B/V, it is found that

$$\frac{pV}{RT} = 1 + \frac{B}{V} + \frac{4B^2}{3V^2} + \cdots$$

[1] R. H. Fowler, Statistical Mechanics, p. 539 (1929).

[2] J. W. Gibbs, Elementary Principles in Statistical Mechanics (1902).

[3] F. G. Keyes, Chem. Rev. **4**, 175 (1929). K. F. Herzfeld, Müller-Pouillets Lehrbuch der Physik, Vol. 3, Kinetische Theorie der Wärme, p. 167.

where the second term may be identified with that of the virial Eq. (1). If, as in the case of helium the molecules are spherically symmetrical

$$B = 2\pi N \int_0^\infty (1 - e^{-\epsilon(r)/kT}) r^2 dr \tag{6}$$

where r is the distance between the two molecules.

Perhaps the most well known of empirical equations of state is that of van der Waals:

$$p = \frac{RT}{V - b} - \frac{A}{V^2}.$$

It is of interest to see what form the intramolecular potential, ϵ, must assume to be consistent with it. The virial Eq. (1) may be transformed into van der Waals' equation if B/V is assumed to be very small relative to unity and

$$B = b - A/RT.$$

If the molecules are treated as rigid spheres of diameter, σ, it is obvious that when $r \leqq \sigma$, $\epsilon = \infty$, and formula (6) yields, after expansion of $e^{-\epsilon/kT}$;

$$B = b - A/RT$$

where

$$b = \frac{2\pi N\sigma^3}{3} = 4 \text{ (total volume of the molecules)}$$

and

$$A = A_0 + \sum_{n=1}^{\infty} A_n/(RT)^n; A_0 = -2\pi N^2 \int_\sigma^\infty \epsilon r^2 dr$$

$$A_n = -2\pi N^{n+2} \int_\sigma^\infty \epsilon^{n+1} r^2 dr.$$

It must be concluded, therefore, that the coefficient A appearing in van der Waals' equation is not a constant, but a slowly varying function of the temperature. This conclusion is born out by experiment in the region of low temperatures where the sum $\sum_{n=1}^{\infty} An/(RT)^n$ may no longer be neglected. Moreover, experiment at high temperatures, invalidates the assumption of rigid molecules. Thus, it is found that b is a slowly decreasing function of the temperature, a fact which can only be explained as due to an interpenetration of the molecules. Van der Waals' equation is therefore to be regarded as merely a first approximation even at small densities.[4]

The Molecular Field

Empirical information furnished by the equation of state suggests that the general character of the force between two molecules may be conveniently represented by means of two potentials, ϵ_r and ϵ_a. The potential ϵ_r, which predominates at small molecular separations, must ascend steeply with in-

[4] F. G. Keyes and R. S. Taylor, J. Am. Chem. Soc. **49**, 896 (1927).

creasing slope as two molecules approach and diminish rapidly as they recede, thus giving rise to a strong repulsive force at small intermolecular distances. The potential, ϵ_a, nullified at small separations by ϵ_r, must fall off less rapidly with the distance, giving rise to an attractive force at larger intermolecular separations. Thus the total intermolecular potential, ϵ, might be written

$$\epsilon = \epsilon_r + \epsilon_a.$$

This representation is to be regarded as more or less schematic, since no sharply defined physical significance can be independently assigned to ϵ_r or ϵ_a. Still, it has the advantage of suggesting two different types of molecular interaction which we believe to be effective in determining the intermolecular energy.

According to present quantum mechanical ideas, the "repulsive" potential, ϵ_r, is to be regarded as arising from a resonance interaction between the molecules. A calculation of the resonance energy has so far been accomplished only for atomic hydrogen[5] and helium.[6] In the case of atomic hydrogen, the situation is complicated by the existence of two alternative modes of interaction, one of them giving rise to the repulsion of which we have spoken, and the other to valence union. Helium is, therefore, the only simple gas for which we have a knowledge of the repulsive field. Although a somewhat complicated function of the interatomic distance, the resonance energy in the range of importance in the thermal interaction of gas molecules may be adequately represented by the formula

$$\epsilon_r = \lambda e^{-cr}.$$

The "attractive" potential is to be regarded as arising from a mutual polarization of the molecules,[7] chiefly due to a rapidly pulsating field associated with the internal motion of the electrons in the molecule. The dominant term in this energy comes from the oscillating dipole. If terms from multipoles of higher order are ignored, the attractive potential has the form

$$\epsilon_a = -\frac{\beta}{r^6}.$$

A general scheme for the calculation of ϵ_a has been developed by London and Eisenschitz.[8] They have made an exact calculation of the mutual energy of two hydrogen atoms as well as rough estimates in the case of some other gases.

[5] Heitler and London, Zeits. f. Physik **44,** 455 (1927); Sugiura, Zeits. f. Physik. **45,** 484 (1927).

[6] Slater, Phys. Rev. **32,** 349 (1928).

[7] In 1920 Debye (Phys. Zeits. **21,** 178, 1920) suggested that the van der Waals attraction in gases had its origin in a mutual electrical polarization. Upon the basis of an electrostatic molecular model, he attempted to calculate the van der Waals A constant for several gases in terms of their electrostatic multipole moments. That his theory was not very successful from a quantitative standpoint, is readily understandable in view of the inadequacy of the molecular model employed.

[8] Eisenschitz and London, Zeits. f. Physik **60,** 491 (1930); London, Zeits. f. Physik **63,** 245 (1930).

[9] Slater and Kirkwood, Phys. Rev. **37,** 682 (1931).

A calculation of the mutual energy of two helium atoms by another method has been carried out by Slater and Kirkwood.[9] They obtain for the total intermolecular potential of helium:

$$\epsilon = \left\{7.7e^{-2.43r/a_0} - \frac{0.68}{(r/a_0)^6}\right\}10^{-10} \text{ ergs} \tag{7}$$

where a_0 is the Bohr radius of the hydrogen atom. In this expression, terms arising from variable multipole moments of higher order than the dipole have been neglected. Moreover, an error of a few percent in the coefficient of the exponential term is not unlikely since an approximate wave function was employed in its calculation.

The Equation of State of Helium

With the expression for the intermolecular potential given by Eq. (7), we have computed the second virial coefficient of helium at several temperatures, by graphical integration of Eq. (6). The results are listed in Table I together

Table I. *Second virial coefficient of helium.*

T (°K)	B (theory) cc/mol	B (H and O) cc/mol
350	10.80	11.60
300	11.14	11.80
250	11.34	11.95
200	11.58	11.95
100	10.75	10.95
20	−6.94	−4.00

with experimental values of Holborn and Otto.[10] The theoretical values of the virial coefficient B have been plotted as a function of the reciprocal temperature in Fig. 1, and as a function of the temperature in Fig. 2. For comparison, the experimental results of a number of investigators have been included.[11,12] From Table I it may be seen that the computed values of the virial coefficient, while consistently lower than the experimental ones of Holborn and Otto, do not differ from them by more than five or six percent between 100°K and 400°K. Below 50°K, the agreement between the two is not quite as close. This fact may probably be attributed as much to error in the experimental measurements as to error in the theoretical values of the virial coefficient. However, a real discrepancy at low temperatures might be expected if the proportion of molecules in quantized collision states became appreciable, for in that event, Gibbs' phase integral would cease to be an adequate representation of the sum of state and Eq. (6) would lose its validity. At present it is impossible to decide whether or not this effect is of im-

[10] Holborn and Otto, Zeits. f. Physik **33,** 1 (1925); **38,** 359 (1926).

[11] Nijhoff, Keesom, and Iliin, Leiden Communications **188C,** Oct. 1927.

[12] Onnes, Leiden Communications, Verslag Akad. Amsterdam **102a,** 495 (1907); **102c,** 741 (1908); Onnes and Boks, ibid **170a, 170b,** (1924); Onnes and Van Agt, ibid **176b,** 625 (1925).

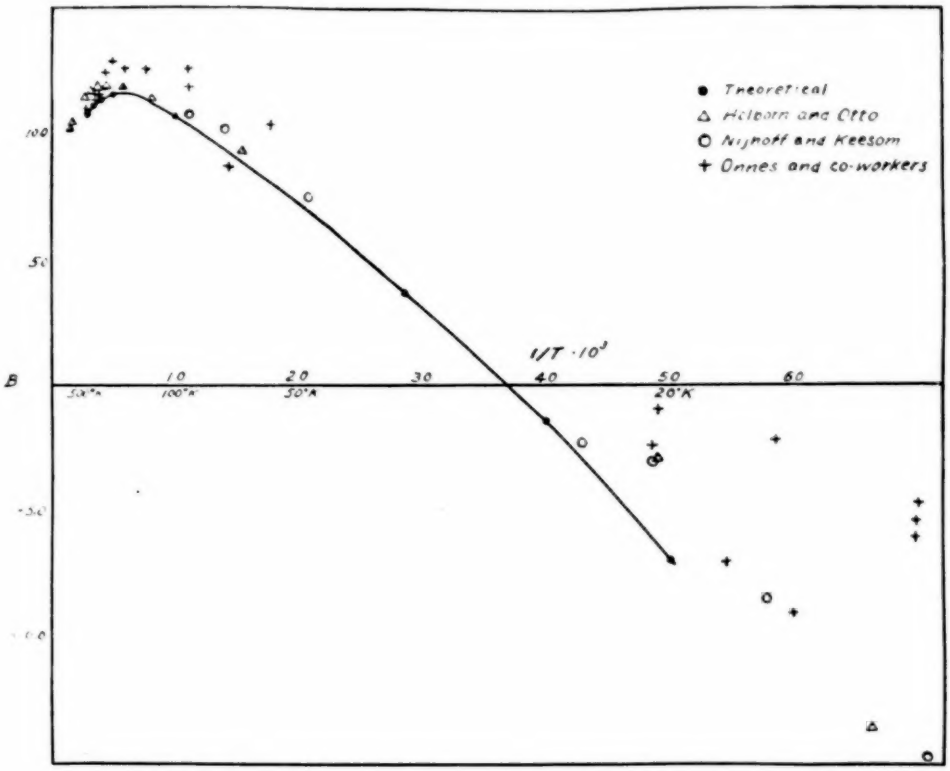

Fig. 1. The second virial coefficient of helium plotted as a function of the reciprocal temperature.

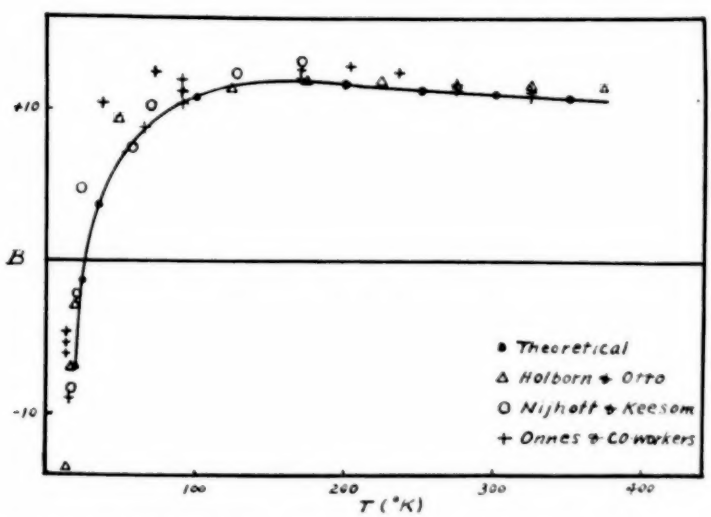

Fig. 2. The second virial coefficient of helium plotted as a function of the temperature.

portance because of inconsistency in the experimental values themselves in the low temperature region.

On the whole the agreement between the theoretical and experimental values of the virial coefficient is extraordinarily good. The slight discrepancy between them is not surprising in view of the approximations which were made in the calculation of the intermolecular energy, Eq. (7).

An examination of Fig. 1 shows that both the theoretical and experimental curves pass through a maximum at about 173°K. This phenomenon has been observed only in the case of helium, but presumably it should occur at sufficiently high temperatures for all gases. Thus, for hydrogen, neon, nitrogen and a number of other gases, the curve obtained by plotting B against $1/T$ shows a decided concave bending in the region of high temperatures. The limitations of van der Waals' equation are clearly brought out in Fig. 1. Below 100°K, it would be possible to apply van der Waals' equation to helium, since in a narrow temperature range the relation between B and $1/T$ may be approximated by a linear function. However, above 150°K, the van der Waals form of equation is entirely inadequate. Not only does the coefficient, A, cease to be constant, but it becomes very sensitive to temperature variation.

Some Properties of Helium

In order to obtain a more detailed comparison with experiment, some properties of helium have been computed with the aid of the theoretically determined virial coefficients. By means of Eq. (1) the pressure has been calculated at several temperatures and volumes. The computed and experimental pressures are given in Table II.

Table II. *Helium pressures calculated from the first three terms of the theoretical virial. Expansion:* $p=(RT/V)(1+B/V+4B^2/3V^2)$.

V (liters/mol)	p (calc.)	p (obs)	Δ
$t=200°C$			
2.000	19.51 atm.	19.52 atm.	−0.01 atm.
0.400	99.60	99.82	−0.22
$t=100°C$			
2.000	15.39	15.40	−0.01
0.333	94.96	95.11	−0.15
$t=0°C$			
2.000	11.27	11.27	0.00
0.250	93.97	94.12	−0.15
$t=-100°C$			
2.000	7.15	7.15	0.00
0.200	75.45	75.66	−0.21

The Joule-Thomson coefficient, μ, may be expressed in terms of the virial coefficient B, and the heat capacity C_p in the following manner:

$$\mu = -\frac{1}{C_p}\left[B + \frac{1}{T}\frac{dB}{d\left(\frac{1}{T}\right)}\right] = +\left(\frac{\partial T}{\partial p}\right)_H \tag{8}$$

At 25°C, μ is calculated to be $-0.061°$ atm.$^{-1}$. Moreover, between $+100°$ and $-100°$C, the value of $dB/d(1/T)$ is extremely small and therefore the temperature coefficient of μ is very small. Roebuck[13] has recently obtained the value $-0.06°$ atm.$^{-1}$ from measurements of the Joule-Thomson effect between $+100°$C and $-100°$C. The temperature variation in μ lay within his experimental error. A rough calculation of the Joule-Thomson inversion point leads to the temperature, 54°K. Although there is no reliable experimental determination with which to compare it the temperature 54°K is in accord with the fact that helium cannot be liquefied at the lowest temperature attainable by evaporating liquid nitrogen, about 70°K.

The thermodynamic temperature scale may be identified with the scale of the ideal gas thermometer. In order to reduce the scale of an actual gas thermometer to the thermodynamic temperature scale, corrections which are functions of the virial coefficients of the gas must be applied. We have used the theoretically determined values of B in conjunction with recent measurements of the coefficient of expansion and the coefficient of pressure of helium[14] to determine the position of the freezing point of water under a pressure of one atmosphere on the absolute temperature scale. The coefficient of pressure of a gas at constant volume is defined as,

$$\alpha_v = \frac{p_{100} - p_0}{100 p_0}$$

where p_0 is the pressure at 0°C and p_{100} the pressure at 100°C. It is easily shown that

$$T_0 = 1/\alpha_0$$

where T_0 represents the position of 0°C on the absolute temperature scale and α_0 is the coefficient of pressure of an ideal gas, for which $pV = RT$. Moreover, it is possible to calculate α_0 in terms of the α_v of an actual gas if its second virial coefficient is known.

$$\alpha_0 = \alpha_v + p_0(6.098B_0 - 4.464B_{100}) \cdot 10^{-7}$$

where p_0 is again the pressure at 0°C, B_{100} the virial coefficient at 100°C expressed in cc/mol, and B_0 its value at 0°C. α_0 may also be obtained from the coefficient of expansion in a similar manner. From the measurements of Heuse and Otto on helium, we compute for the average value of α_0.

$$0.0036609 \text{ atm./°}$$

which corresponds to

$$T_0 = 273.16.$$

By linear extrapolation Heuse and Otto find that

$$T_0 = 273.16.$$

The International helium thermometer is defined as a constant volume gas thermometer in which the pressure of helium at 0°C is equal to that of a

[13] J. R. Roebuck and H. Osterberg, Phys. Rev. **37**, 110 (A) (1931).
[14] W. Heuse and J. Otto, Ann. d. Physik [5] **2**, 1012 (1929).

one meter column of mercury at 0°C and standard gravity. The gas temperature is defined as

$$t_g = \frac{p_{tg} - p_0}{p_{100} - p_0}.$$

The corresponding temperature on the absolute scale is of course

$$t = T - T_0.$$

The correction Δt which must be added to the gas temperature t_g to bring it into agreement with the absolute temperature scale may be computed from the second virial coefficient by means of the formula

$$\Delta t = 5.870\{3.731t_g(B_{100} - B_0) - (373.1 + t_g)(B_{tg} - B_0)\} \cdot 10^{-5}$$

where the virial coefficients B_{100}, B_0, and B_{tg} are expressed in cc/mol. The corrections have been calculated for several temperatures. They are listed with those given by the Reichsanstalt in Table III.

TABLE III. *Corrections to international helium thermometer scale.*

t_g	Δt (calc.)	Δt (H and O)
200	+0.006	+0.008
100	0.000	0.000
50	−0.0003	−0.001
0	0.000	0.000
−100	+0.009	+0.009
−200	+0.032	+0.028
−250	+0.051	+0.043

L. Holborn and J. Otto, Zeits. f. Physik **38**, 359 (1926); **30**, 1 (1925).

Baxter and Starkweather[15] have measured the density of helium. Their value at 0°C and a pressure of one international atmosphere (pressure of a column of mercury 76 cm in height at 0°C and at standard gravity; $g = 980.665$ dynes sec^{-2}) is

0.17847 g/liter.

Using this density together with our value of B at 0°C and taking the gas constant, R, as 0.08206 liter atm. the mean for a large number of gases, we calculate the atomic weight of helium as 4.0022. This is to be compared with the atomic weight 4.0020 obtained by Baxter and Starkweather from the density given above and their own compressibility measurements at low pressures.

In all of the cases which have been considered, the theoretically determined virial coefficient gives results which are in substantial agreement with experiment. When it is remembered that the calculation of the virial coefficient is based upon purely *a priori* considerations and depends upon experiment only through the values of certain universal atomic constants, it seems to furnish a striking confirmation of the present theory of intermolecular forces.

[15] Baxter and Starkweather, Proc. Nat. Acad. Sci. **11**, 231 (1925).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

Mass Defects of C^{13}, O^{18}, N^{15}, from Band Spectra, and the Relativity Relation of Mass and Energy

Chadwick, Constable and Pollard,[1] in a recent article, give on page 482 a plot of the "mass defect" of a number of atomic species, as a function of the number of α-particles in the nucleus. It is of considerable interest to add to this plot certain atomic species recently discovered by means of band spectra. In the case of C^{13}, O^{18} and N^{15}, the mass of the new isotope, relative to the mass of the more abundant species, has been calculated from the band spectra data. Thus King and Birge[2] find that the mass of C^{13} relative to C^{12} is 13:12 exact, to about one part in 10,000. The mass defect plot just mentioned is based on the atomic masses obtained by Aston.[3] Accepting his results, one obtains 10.7×10^{-3} as the mass defect of C^{13}. (Henceforth all mass defects will be given in 10^{-3} mass units). This result is given (as 11×10^{-3}) in a footnote, page 481 by *C.C.P.*

For O^{18} Babcock and Birge[4] have obtained a mass of 18.0065, based on $O^{16}=16$ exactly, which is also Aston's basis. The probable error is only about one part in 10^5. The resulting mass defect of O^{18} is 17.7.

Herzberg[5] has obtained the mass ratio N^{15}/N^{14}, from his measured isotope shift for the heads of the 1–0 and 2–0 bands of the second positive group of nitrogen, the molecules concerned being $N^{15}\cdot N^{14}$ and $N^{14}\cdot N^{14}$. The measured shifts are appreciably less than his calculated values, but unfortunately he made a theoretical error in his calculations which definitely affects his conclusion. All isotope shifts are expressed as a function of (ρ^n-1) where n is some positive integer. $\rho=(\mu_1/\mu_2)^{1/2}$ and μ, is the reduced mass of the *more* abundant molecule. Thus for the band systems containing O^{18}, C^{13} and N^{15}, the value of ρ is *less* than unity, and the vibrational shift is to the red, for bands located on the violet side of the origin of the system.

Herzberg, however, calculated ρ as $(\mu_2/\mu_1)^{1/2}$ and so obtained a value greater than unity. This leads not only to a shift in the direction opposite to that observed, but also to an incorrect absolute magnitude. In order to obtain the calculated shift Herzberg made new measurements of certain band heads of this system. He thus derived a new vibrational energy function $f(v')$ for the upper state, and combined this with the writer's $f(v'')$ of the lower state, to get an energy equation of the system. Birge and Sponer[6] had already given a $f(v')$ for this system, based on all available data, reduced where necessary to the I. A. system. The two $f(v')$ appear somewhat different, but fortunately lead to practically the same calculated vibrational shifts for the $1-0$ and $2-0$ bands. The correct value of ρ, assuming even 14 and 15 masses, is 0.98319, and the vibrational shifts are, from the Birge and Sponer equation, -35.16 and -65.79 cm^{-1}, and from Herzberg's equation, -35.19 and -65.72 cm^{-1}. It seems best to adopt the average values -35.17 and -65.76 cm^{-1}.

Since a fine structure analysis of these two bands has not been carried out, one must use for the rotational isotope shift the sufficiently

[1] J. Chadwick, J. E. R. Constable and E. C. Pollard, Proc. Roy. Soc. **A130,** 463 (1931). To be called *C.C.P.*

[2] A. S. King and R. T. Birge, Astrophys. J. **72,** 19 (1930).

[3] F. W. Aston, Proc. Roy. Soc. **A115,** 487 (1927).

[4] H. D. Babcock and R. T. Birge, (abstract) Phys. Rev. **37,** 233 (1931).

[5] G. Herzberg, Zeits. f. phys. Chemie **B9,** 43 (1930).

[6] R. T. Birge and H. Sponer, Phys. Rev. **28,** 259 (1926).

accurate approximation $(\rho^2-1)\nu_m$, where ν_m is the distance from the origin to the head, for the *middle* component of the triplet series found in these bands. Fortunately the desired origin can be located, by mere inspection, on spectrograms of an "effective low temperature" source. The resulting rotational shifts, as given by Herzberg, are $+0.6$ cm^{-1} and $+0.8$ cm^{-1} respectively, corresponding to *origin-head* distances of 18 and 24 cm^{-1}. (This distance in the $0-0$ band is 13.3 cm^{-1}, according to the writer's fine structure analysis.)

Now the $f(v')$ to which reference has been made are based on measurements of the heads, and are slightly in error, due to the varying distance of origin to head. The resulting correction to the vibrational shift I find to be -0.08 and -0.18 cm^{-1}, for the $1-0$ and $2-0$ bands, respectively. The final calculated shifts for the *heads* are then -34.65 and -65.14 cm^{-1}, as compared with Herzberg's *observed* shifts -34.6 and -64.6 cm^{-1}. One thus obtains the result that the mass ratio N^{15}/N^{14} is *less* than 15/14 by one part in 10,000, and one part in 1700, from the $1-0$ and $2-0$ bands, respectively. Then, using Aston's value $N^{14}=14.008$, one obtains $N^{15}=15.0065$ and 14.999 respectively. From these figures there results a mass defect for N^{15} of 23.3 and 30.6, or an average value of 27.0

We may now place these mass defects on the plot previously mentioned. The C^{13} defect (10.7) lies just above the value obtained from α-ray disintegration experiments (given as 9.9 by *C.C.P.* but calculated as 9.8 by the writer). This mass defect, 9.8, is obtained from Aston's mass defect 6.38 for B^{10} combined with an energy loss equivalent to 3.42 (in 10^{-3} mass units), as observed by *C.C.P.* in the transformation $B^{10}\rightarrow C^{13}$. The close agreement of the two mass defect values for C^{13} (10.7 and 9.8) is of more than passing interest, for it constitutes a *very* rough, but direct experimental check of the accepted relation between mass and energy $\Delta E=c^2\Delta m$. So far as I am aware, it is the first experimental check by this very direct method.

The mass defect for O^{18} (17.7) may be compared with that for O^{17} (12.6), as evaluated by *C.C.P.* from their disintegration experiments,[7] for O^{16} (8.64). The fact that these three points (corresponding to masses of 18.0065, 17.0029 and 16.0000) are nearly equally spaced is probably significant. The spectral data for O^{17} are very meager, as compared to O^{18}, but the mass of O^{17} is now being calculated from such data and the result, if of sufficient accuracy, will constitute a second check on the mass-energy relation.

Finally, the mass defect of N^{15} should lie on the curve passing through B^{11}, F^{19} etc. The predicted value, from the published curve, is 24.5, agreeing well within limits of error with the average observed value of 27.0. Other interesting relations may be deduced from the mass defect graphs published by *C.C.P.* but it is the primary purpose of this letter merely to locate on these graphs the new data for C^{13}, O^{18} and N^{15}.

RAYMOND T. BIRGE

University of California,
March 4, 1931.

[7] The first calculation of the mass of O^{17} by such a process, with the result 17.0033 ± 0.0009, was made by W. F. Giauque, Nature **124,** 265 (1929).

Momentum Transfer to Cathode Surfaces by Impacting Positive Ions in a Helium Arc

The present problem was suggested by K. T. Compton and may best be introduced by the following quotation from one of his papers (Phys. Rev. **36,** 706, 1930). "Although, as we have seen, the impact of a charged ion against the cathode contributes nothing to the pressure against it (on account of the counterbalancing pull during its attraction to the cathode), nevertheless if the neutralized ion leaves the cathode with any momentum there is imparted to the cathode an equal opposite momentum." In the experiment here reported this hypothesis is tested by studying the momentum imparted to an auxiliary cathode in a helium arc.

The auxiliary cathode (or plane collector) was suspended from a vertical side tube in the negative glow of a hot cathode helium arc. The collector was a flat molybdenum plate one centimeter in diameter, insulated on one side by a glass plate. This collector was nonvolatilizing so that there was no possibility of a pressure as a result of a stream of metal vapor leaving the collector. The suspension consisted of a long period glass pendulum supported on two steel points and carrying a small

mirror. Thus by means of the deflection of a light beam, small forces on the collector could be measured. The forces were determined as a function of the negative potential applied to the collector using several different values of the total current through the arc.

From the data obtained the calculation of an accommodation coefficient for helium positive ions is quite simple if corrections for the current that reaches the collector at its edges are neglected. Let β be the fraction of the incident energy of the ion which is retained after neutralization. β is approximately equal to $1-\alpha$ where α is the accommodation coefficient. Assuming that the neutralized ions escape in random directions, the pressure on the collector is given by

$$P=\frac{i}{2e}(2meV\beta)^{1/2}$$

where P is the pressure exerted on the collector, i the positive ion current density, e the charge, m the mass of a helium ion and V the negative potential of the collector with respect to the surrounding space. Putting in the constants,

$$\beta=\frac{4.63(10^3)P^2}{i^2V}$$

where P is in milligrams per square centimeter, i in milliamperes per square centimeter and V in volts. α follows immediately from the relation $\beta=1-\alpha$.

When a small correction for edge effects is included preliminary results indicate a value of about 0.5 for α. In further work the elimination of edge effects will be attempted and the experiments continued using a number of other gases.

EDWARD S. LAMAR

Palmer Physical Laboratory,
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Princeton, N. J.,
March 9, 1931.

Raman Spectra of Silico-Chloroform

We have been investigating the Raman spectra of silico-chloroform and have succeeded in observing a number of its Raman frequencies and particularly that characteristic of the Si-H-bond. The spectra were observed by illuminating with a mercury arc a tube filled with the liquid immersed in liquid ammonia contained in an unsilvered Dewar flask. The light was reflected from the top of the tube into a Hilger D78 glass spectrograph.

The frequencies which we have observed together with those of chloroform (Proc. Roy. Soc. **A127,** 360 (1930)) are shown in the following table:

$CHCl_3$	$SiHCl_3$
261 (5)	179 (strong)
367 (6)	250 (strong)
669 (6)	489 (very strong)
762 (3d)	587 (strong diffuse)
1218 (2d)	799 (strong diffuse)
1441 (1)	——
3019 (3d)	2258 (strong diffuse)

It is to be noted that we observe six frequencies which can be correlated with those of chloroform, the frequencies of silico-chloroform being always smaller than those of the other compound. We have been unable to detect the seventh frequency which should be the weakest of the frequency displacements. The highest frequency which we observe, namely, 2258, is that which corresponds to the frequency usually assigned to the vibration of the proton along its valency bond with respect to the carbon atom in chloroform; so that it is to be interpreted as a similar vibration of the hydrogen atom with respect to the silicon atom along the Si-H-bond.

The differences in these two frequencies can be due only to the difference in the restoring force constants for the two cases, for the effective mass in both cases should be approximately the mass of the hydrogen atom. We have also been able to observe both positive and negative displacements for the lower frequencies from the yellow lines of mercury in addition to those more easily observed from the blue and violet lines. Complete details of this investigation and that of other compounds of this type will be reported at a later date.

HAROLD C. UREY
CHARLES A. BRADLEY, JR.

Department of Chemistry,
Columbia University,
March 11, 1931.

New Lines in the Near-Infrared Spectrum of the Neutral Hg Atom

Thirty-nine new lines have been observed in the region 0.9μ to 2.25μ with an automatic recording spectrograph[1] of the Littrow type using the equivalent of five 60° prisms. The lines are extremely weak so that an effective slit-width of approximately 15 A° was necessary for detection with a single junction thermocouple. The intensities of these lines are of the order of 0.002 that of the strong line at 1.0142μ, which gave a 45 cm scale deflection at 4 meters. The arc was operated at 86 volts and 3.8 amperes.

Wave-length standards were taken from E. D. McAlister's report (Phys. Rev. **34,** 1142–1147, Oct. 15, 1929) and T. Takamine's and T. Suga's report (Inst. Phys. and Chem. Research Tokyo, Sci. Papers No. 232, March 20, 1930). All the lines in the region 0.9 to 1.0μ, observed photographically by Takamine and Suga were discernible, and the line at 0.940μ resolves into two, 0.9432 and 0.9447μ. The line at $2.108\mu \pm 10^{-3}$ is of the same intensity as the one 2.2489μ observed by F. Paschen, and the wave-length uncertainty is due to the fact that the nearest known line is 1300A away.

This brings the number of lines in this spectral region, 0.90 to 2.25μ, to a total of 96.

New HgI Lines and Possible Classification.

No.	λ	ν	Classification
1	0.9253	10807.3	
2	0.9432	10602.2	$2^1P_1-6^1D_1=10600$
3	0.9447	10585.4	$2^1P_1-6^3P_2=10581$
4	0.9697	10312.4	
5	0.9774	10231.0	$2^3P_0-2^1F\ =10231$
6	0.9780	10225.0	$2^3P_0-2^3F\ =10227$
7	0.9918	10083.0	$2^1D_1-5^3S_1=10083$
8	0.9983	10017.	$2^3P_1-4^3D_1=10016$
9	1.0211	9793.3	
10	1.0240	9765.6	$2^1P_1-5^1D_1=9764$
11	1.0276	9731.4	$2^1P_1-5^3P_2=9730$
12	1.0294	9714.4	$2^3P_1-4^3P_0=9713$
13	1.0307	9702.1	
14	1.0361	9651.5	$2^3D_2-5^3D_3=9654$
15	1.0436	9582.2	$2^1D_1-5^3P_1=9583$
16	1.1008	9084.3	
17	1.1018	9076.0	$2^3S_1-9^3P_1=9078$
18	1.1036	9061.2	$2^3P_2-4^3S_1=9060$
19	1.1129	8985.5	$1^3S_1-2^3D_1=8986$
20	1.1363	8800.4	$2^3S_1-8^3P_1=8805?$
21	1.1433	8746.6	
22	1.1790	8481.7	$2^3P_2-4^3D_2=8482$
23	1.1916	8392.1	$2^1P_1-4^3D_2=8397?$
24	1.2193	8201.4	$^3P_2-3^3D_1=8200$[2]
25	1.2224	8180.6	$2^3D_2-4^3P_2=8180$
26	1.2376	8080.1	$2^1P_1-4^3P_0=8082$
27	1.2440	8038.5	$2^3D_1-4^3P_0=8039$
28	1.3634	7334.3	
29	1.3979	7153.6	$2^3P_1-3^3P_2=7161?$
30	1.4027	7129.1	
31	1.4127	7078.6	$2^1D_1-4^1S_0=7068?$
32	1.4160	7062.1	$2^3S_1-5^3P_2=7062$
33	1.7269	5790.7	$2^1P_1-3^3D_1=5791$
34	1.7696	5651.0	$3^3P_1-6^3S_1=5656?$
35	1.7980	5561.7	$3^3F\ -8^1D_1=5563$
36	1.8084	5529.7	$2^1P_1-3^3P_2=5530$
37	1.9481	5133.2	$2^1D_1-3^3P_1=5134$
38	1.9571	5109.6	$2^3D_1-3^3P_0=5110$
39	2.1080	4744	$2^3P_1-3^1S_0=4742$

[1] Constructed by E. D. McAlister, Smithsonian Institute.

[2] Takamine's x-term given by F. Paschen as a $^3P_2$-term that may assume two different values.

H. J. UNGER

Department of Physics,
University of Oregon,
March 10, 1931.

Spark Spectrum of Caesium (Cs II)

In pursuance of the systematic investigation of the alkali spark spectra by means of the hollow cathode excitation (Phys. Rev. **36,** 219, 1931) we have now carried the analysis to the first spark spectrum of caesium. Contrary to Rb II, the excitation of the caesium hollow cathode discharge in helium is about two volts more than sufficient to produce excitation of all the levels of the caesium ion so that higher members of the resonance series were excited and a total of eight lines appeared in the vacuum region (see table below).

Int.	λ	ν	Spectroscopic Origin
(20)	926.75	107905	$5p^6-5p^5(^2P_{1\frac{1}{2}})6s$ and $5d$
(20)	901.34	110946	
(20)	813.85	122872	$5p^6-5p^5(^2P_{\frac{1}{2}})6s$ and $5d$
(20)	808.77	123645	
(12)	668.43	149604	
(5)	657.15	152172	$5p^6-5p^5(^2P_{1\frac{1}{2}})$ $7s$ and $6d$
(12)	639.42	156392	
(7)	612.82	163180	$5p^6-5p^5(^2P_{\frac{1}{2}})$ $7s$ and $6d$

With the separation of these lines as a guide, it has been possible to interpret the classification of the Cs II lines in the visible region as given by Sommer (Ann. d. Physik **75,** 163, 1924). The energy level scheme given by this author is correct but incomplete. For, due to the large separation of the $5p^5$ (^2P) term of Cs III, the energy levels of each configuration are split up into two distinct groups according to whether they are built upon $^2P_{1\frac{1}{2}}$ or upon $^2P_{\frac{1}{2}}$. Sommer's classified lines are to be interpreted (α) as transitions from five of the six levels of the configuration $5p^5$ ($^2P_{1\frac{1}{2}}$) $6p$, to five of the ten levels of the configurations $5p^5$ ($^2P_{1\frac{1}{2}}$) $6s$ and $5p^5$ ($^2P_{1\frac{1}{2}}$) $5d$, (β) as transitions from eight of the ten levels of the configurations $5p^5$ ($^2P_{1\frac{1}{2}}$) $7s$ and $5p^5$ ($^2P_{1\frac{1}{2}}$) $6d$ to the aforesaid five levels of $5p^5$ ($^2P_{1\frac{1}{2}}$) $6p$. No levels built upon $^2P_{\frac{1}{2}}$ were found by Sommer, but the present data give clear indications concerning their position. In the above table, the intensities, wave-lengths, and frequencies of the resonance lines are given as well as their spectroscopic origin.

The resonance potential corresponding to the two strongest lines 926.75 and 901.34 is equal to 13.32 and 13.70 volts, respectively.

Otto Laporte
George R. Miller
Ralph A. Sawyer

Department of Physics,
University of Michigan,
Ann Arbor, Michigan,
March 16, 1931.

Hyperfine Structure and Incomplete Polarization of Mercury Resonance Radiation

The author has made studies of the Zeeman effect of the mercury resonance line in absorption and has shown, that for certain intensities of the magnetic field mercury vapor transmits, from the five hyperfine-structure components of the 2537A-line: (1) only the outer short wave-length component, −25.4 mA, or (2) one inner and one outer component, −10.4 and +21.5 mA, or (3) two inner components, 0 and +11.5 mA. Further the author has determined the absorption coefficients and the life-times of the mercury atoms excited with the above mentioned filtered radiations. A full account appeared in Bull. Acad. Pol. Nov.–Dec. p. 464, 1930; preliminary communications in Nature, Nov. 1, 1930, and Phys. Rev. Nov. 15, 1930.

Recently the author has extended the investigations on the hyperfine structure of the resonance radiation excited with these filtered radiations. These investigations now in progress show, that by excitation with the outer component −25.4 mA alone, there appears in emission only the same component, that is, we have to deal with a pure monochromatic resonance effect. It is to be seen on the accompanying photographs obtained with a Lummer-Gehrcke parallel plate, from which the first shows the five-fold structure of the resonance radiation excited with the unfiltered radiation of the mercury vapor arc, the second, the single structure of the same radiation obtained by the excitation with the −25.4 mA component alone.

The experiments made up to the present on other components seem to show, that in general each of the five components gives a pure resonance effect, consequently there are no hyperfine levels of the 2^3P_1-energy level from which more than one component can be emitted.

The results communicated above and those from investigations of the Zeeman effect show that the five-fold structure of the 2537A line is due rather to the isotope effect than to a magnetic moment of the nucleus. At the same

Fig. 1.

Fig. 2.

time they give interesting views concerning the cause of the incomplete polarization of the mercury resonance radiation in absence of magnetic field.

In the first place, according to the supposition of Olson (Phys. Rev. **32,** p. 443, 1928), the degree of polarization must depend on the relative intensity of the components in the exciting light. Further, in the case of the excitation with the outer -25.4 mA component, previously investigated by the author, one should expect that the degree of polarization should be about 32 percent (in comparison with 50 percent by excitation with all five components). This difference is so small that I could overlook it in the approximate estimations of the visibility of the interference fringes (I did not take into account the dependence of the plate density upon the time of exposure). It must be remarked that experiments made recently by A. Ellett and described by him in a letter in the January 15th issue of this Review do not contradict the results of my investigations. From Fig. 2 of my paper (Bull. Acad. Pol. l.c.) it is to be seen, that under the conditions chosen by Ellett (2000 gauss) the filtering absorption cell does not transmit the outer -25.4 mA component; the resonance radiation is excited probably not with cores, but by the transmitted wings of the hyperfine-structure components.

As regards the other experiment, on the basis of which Ellett supposes that the parallel Zeeman component of the outer long wavelength component ($+21.5$ mA) is shifted by the magnetic field, it must be remembered, that such a shift is not detected either in emission (McNair) or in absorption (the author, l.c.). On this account I think that another explanation should be sought for this experiment of Ellett. It is possible, for instance, that the whole effect could be explained by the relatively large difference of the absorption coefficients for the inner and the outer components.

S. Mrozowski

Physical Laboratory of the Society
of Sciences and Letters, Warsaw,
March 2, 1931.